THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII JUNE 1957 No. 6

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII JUNE 1957 No. 6

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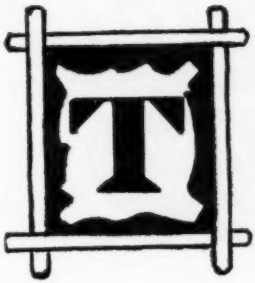

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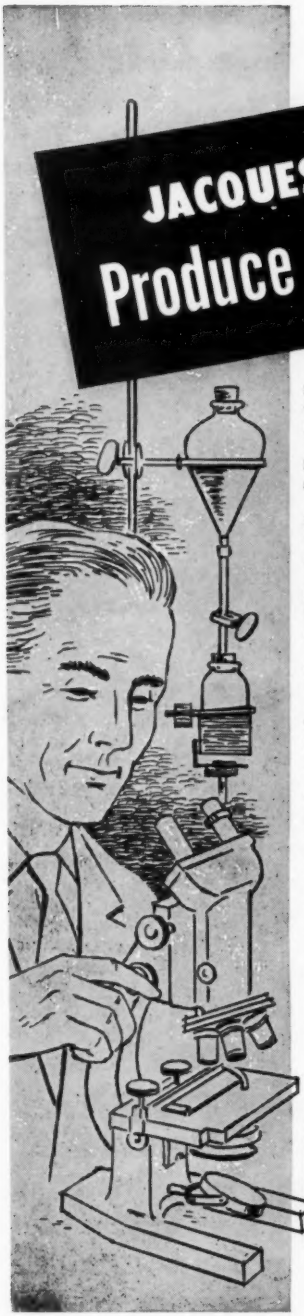

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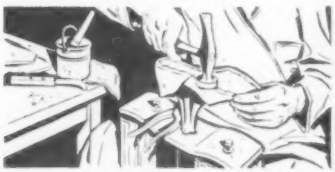
For more information on new LEUKANOL C and our many other leather chemicals and services, write to the Leather Chemicals Department or contact one of our many field representatives.



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1957: Edition 2

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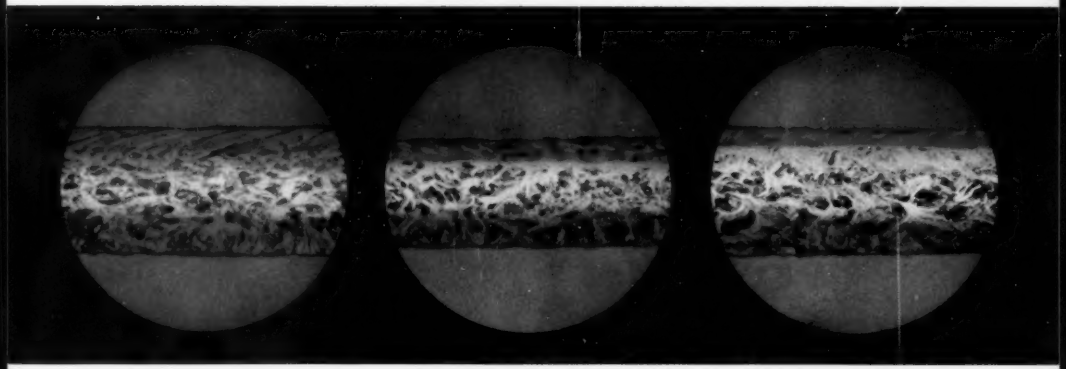

MOBILTAN 275

This carefully compounded fatliquor gives excellent results in both full and pasted leathers. It is light-fast and compatible with resin re-tannages. Special qualities permit surface nourishment with enough penetration to give desired mellowness.

MOBILTAN A

As photo shows, this highly sulphonated oil completely penetrates skins, imparting permanent lubrication to innermost fibres. It leaves a clear grain free of raw oil and can be used on a variety of skins including soft upper leathers.

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There's a Mobil Product Bulletin completely describing every Mobil tanners product!

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WHAT IT IS:
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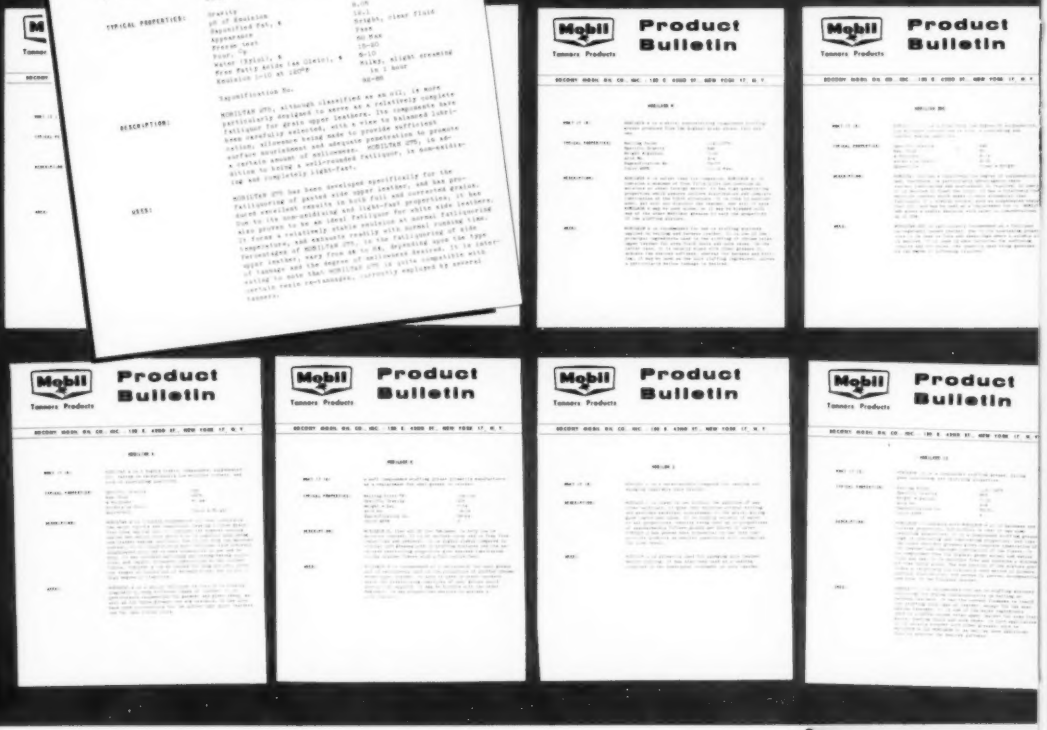
USES:

Perhaps there's a Mobil tanners product that can solve one of your tanning problems. Simply state the type of product you are interested in, and we will send you a Product Bulletin completely describing the product we feel will fill your need. Use the handy blank provided below.



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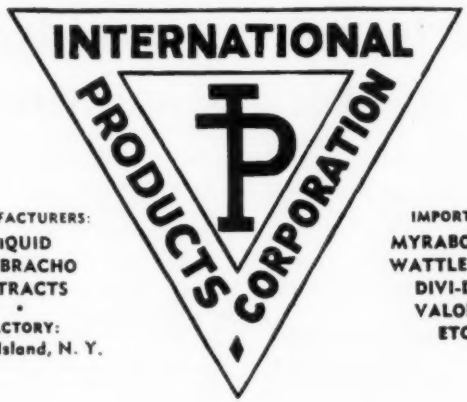

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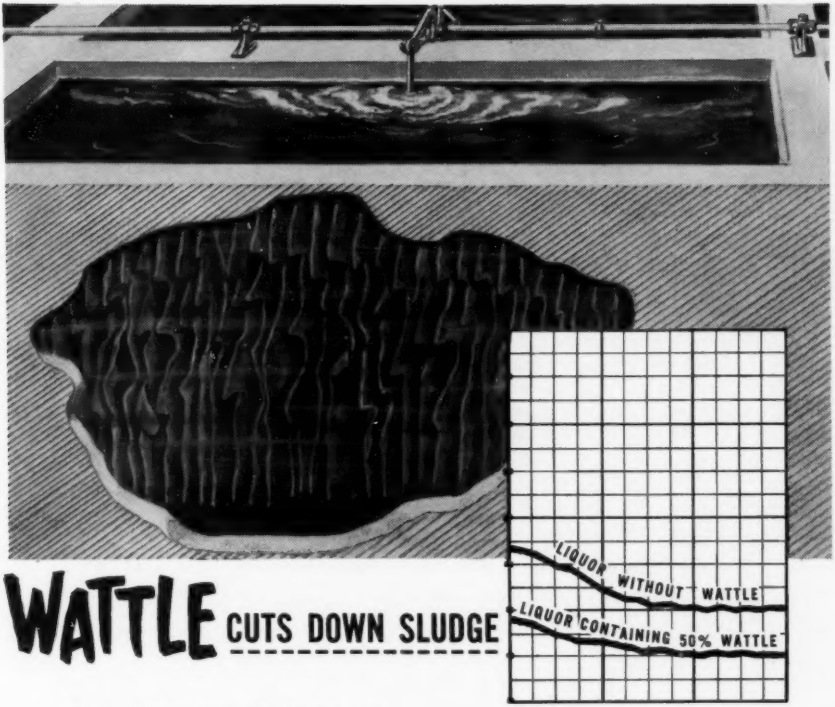

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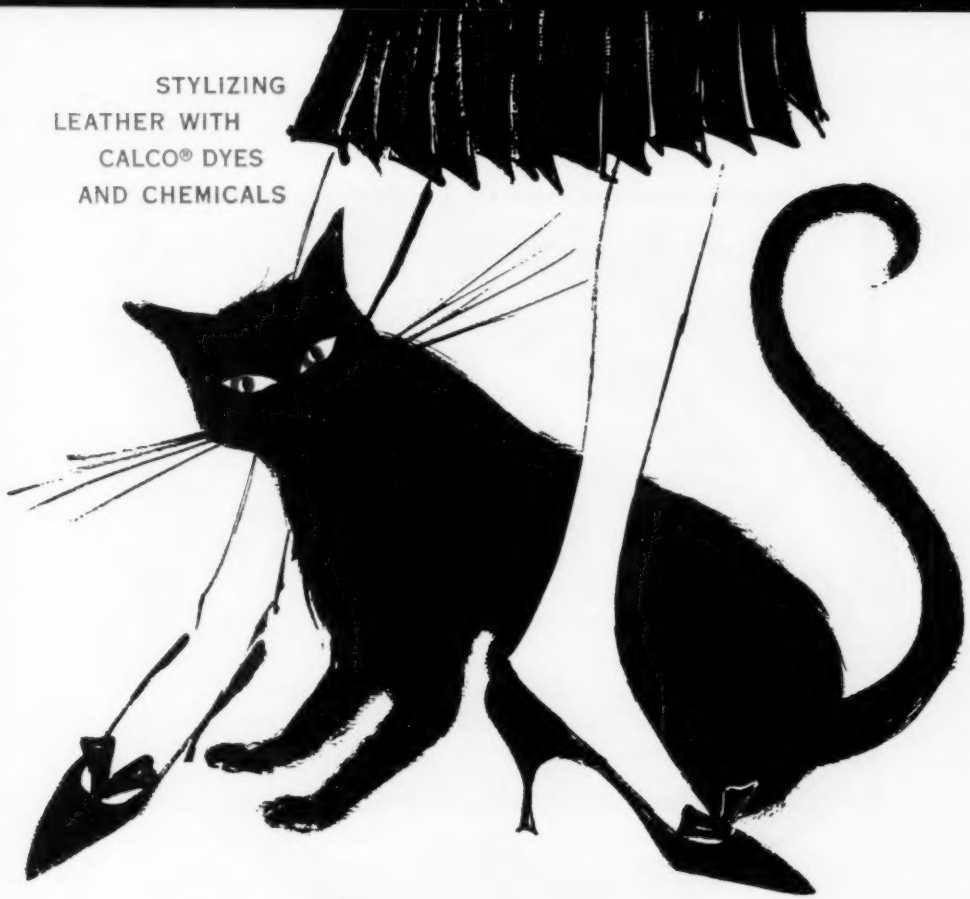

for Suede
for black
for beauty

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CALCO DEVELOPER MTD

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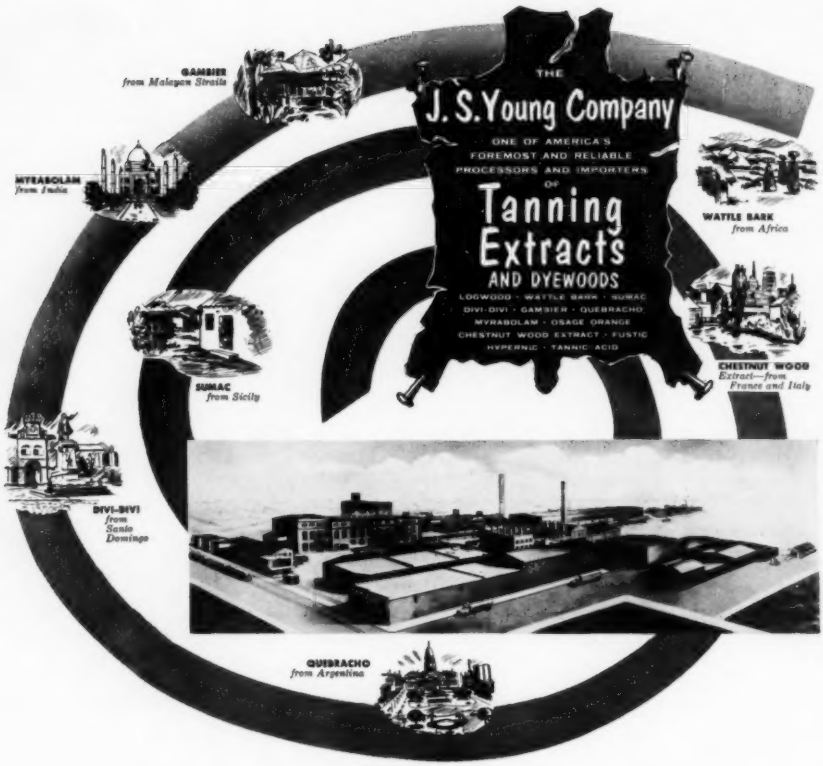

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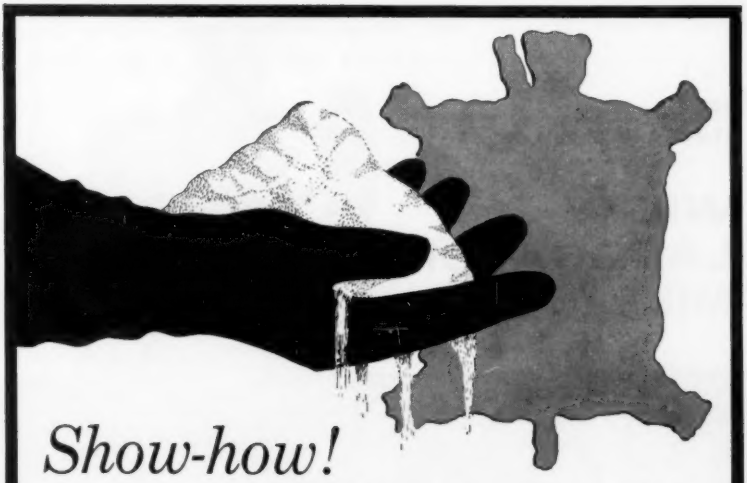

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JOURNAL OF THE
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Vol. LII JUNE 1957 No. 6

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PRACTICAL BATING. THE EFFECT OF BATING VARIABLES ON SIDE AND CALF LEATHER QUALITIES*

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ABSTRACT

Results of practical bating trials in six tanneries are reported. The tests were made on full-scale production lots, and the results are reported in terms of effects on individual properties of the leather, such as break, temper, drawn grain, etc. Variables studied include quantity and type of enzyme, temperature and time of bating, and deliming conditions. The results obtained in the different tanneries are in excellent agreement.

INTRODUCTION

Studies of bating reported in the literature have been numerous indeed, and yet in terms of leather qualities important to the practical tanner very little information is available. By leather qualities we mean characteristics such as temper, smoothness of the grain, break of the grain, fullness, etc., by which a tanner judges his production. The literature abounds in methods for testing bating enzymes for strength, but, with few exceptions, none of these papers attempt to prove the particular method in terms of realistic effects on leather; yet this alone is really the only reason for wanting such a method in the first place.

We would like to consider bating, not as an isolated chemical reaction of enzymes with protein systems, but as an important practical process necessary for the manufacture of high-quality calf and side leather. We restrict ourselves to calf and side leather since the very different bating processes that are used for other types of leather, such as kid and sole, have not been investigated. With this viewpoint of practical bating in mind we can proceed to a definition of the problem and a decision as to how to obtain the required information.

The most important question to be answered is: What effect is produced by the regular bating process in terms of leather qualities? Commercial

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bating is really two combined processes, one the deliming action and the other the enzyme action, and therefore these effects must be in some way separated if we are to be able to answer the primary question adequately. This can be most easily done by first holding the deliming action constant and varying the enzyme treatment, and then reversing the procedure. This, of course, does not tell us about the secondary effects of one upon the other, but at least it gives us information about the main effects.

One of the most discouraging aspects of most practical tannery experimentation is that results obtained in one tannery do not always apply to another tannery, and therefore most practical tanners look with considerable doubt upon results of experiments coming from some tannery other than their own. In order that this work might be acceptable to the industry and in our own group of tanneries, it was decided to run the same experiment in all six tanneries with each report being made without knowledge of the results from any of the other tanneries.

Another factor contributing to the general lack of confidence in tannery tests is that small-scale tests do not always produce the same results as regular large-scale production operations. To avoid this, almost all tests reported in this paper were conducted on full-production packs in regular tannery operations. The method of evaluating the results of tests varied considerably from tannery to tannery but in each case represented the best method in the opinion of the tannery involved for determining the change in leather qualities produced. Some tanneries preferred a matched side method (better or worse), and some used a subjective scale (good, fair, and poor). In all cases the evaluations were done with no knowledge of which side or skin was in the experiment and which in the control, so that all results are free of this possible bias. A full description of each method of evaluation is given in the Appendix at the end.

EFFECT OF THE ENZYME IN BATING

As previously mentioned, the primary object was to determine exactly what effect the normally used enzyme had in terms of leather qualities. It was decided that this could best be accomplished by comparing zero enzyme and regular delimer with the standard amount of enzyme used in regular production, as well as ten times the normal enzyme and regular delimer with standard production. These tests, therefore, were run in all six tanneries in full-production packs according to the procedures outlined in Table I and were carefully evaluated for various leather qualities as shown in Table II. The evaluation methods used are described in the Appendix.

The results show an amazing correlation of evaluation among the six tanneries and certainly enable us to get a very clear-cut picture of the effect of the enzyme in bating calf and side leather.

TABLE I

EXPERIMENTAL SET UP FOR ZERO ENZYME, NORMAL ENZYME, AND TEN-FOLD ENZYME TESTS

(Regular amount of delimer used in all tests.)

	Tannery "A"	Tannery "B"	Tannery "C"
Stock	30/35 lb.-hides—enough for 4 full drum loads	120 calfskins of same weight, size, and quality	150 selected 9/12 packer calfskins
Design experiment	40 matched sides in each test and control pack; enough regular stock added to make full drum load	120 skins processed thru beamhouse together; separated and bated in separate paddles; tanned together in same drum along with enough regular stock to make a full drum	Randomly sorted into three tests. Regular stock added to make full packs. Processed separately thru beamhouse and bating, then sorted out and all three tests tanned together
Processing and evaluation	Run through processing as separate packs; staked to uniform temper; evaluated before buffing by matched-pair method	All tests processed together in one drum; evaluated prior to finishing by ranking method	All tests processed as one load; wet-staked all alike; evaluated after finishing by good, fair, poor scale
Type of leather produced	Full chrome, lightly veg. mordanted, fatliquored, corrected grain	Full chrome, pasted, black calf	Full chrome, pasted, black calf

	Tannery "D"	Tannery "E"	Tannery "F"
Stock	Regular stock	Hides selected to make M and MH sides and extremes	Enough hides to make 10,000 lb. white wt. for M- wt. leather
Design of experiment	140 sides crisscrossed and matched; set up into 3 test packs of 47 sides each; enough regular stock added to bring each load to 7000 lb. All sides processed through beamhouse together	Preliminary zero enzyme test run with 20 matched sides; main zero enzyme run with 65 matched sides; 10-fold enzyme run with 56 matched sides. All loads made up to 4800 lb. with regular stock. All sides processed through beamhouse on same equipment	Four matching packs of 2500 lb. each set up into two test and two control packs

TABLE I — (Continued)

	Tannery "D"	Tannery "E"	Tannery "F"
Processing and evaluation	Run as separate packs; staked to uniform temper; evaluated after finishing by matched pair method	Preliminary zero enzyme fatliquored in same drum. Main tests fatliquored separately. Mechanical work done on mixed controls and tests. Evaluated after wet staking by matched side method	Sorted in blue into various leathers. Processed as separate packs. Evaluated before staking and after finishing by good, fair, poor scale
Types of leather produced	Full grain, full chrome; corr. grain, veg.-retanned; corr. grain, veg.-retanned, stuffed	chrome-retanned, lightly veg.-mordanted, corr. grain	HM corr. grain, veg.-retanned; LM corr. grain, chrome-retanned, lightly mordanted

Effect on drawness.—The most positive evidence of the effect of the enzyme is that on drawness, where all six tanneries agree almost exactly. Increasing the enzyme from zero to the amount normally used by the tannery reduces the drawness of the leather. Above the normal level of enzyme four tanneries found no further decrease in drawness, but two tanneries found evidence for still further reduction in this undesirable characteristic.

Effect on temper.—The evidence of the effect on temper is almost as strong as it is on drawness. Five tanneries found that the zero enzyme test was firmer than the regular process, and the other tannery found that the regular process leather was firmer than the ten-fold enzyme test. In general we can say beyond doubt that the use of enzyme in bating produces a softer leather than zero enzyme, and that this effect was not overcome even in those tanneries where the staking was done to optimum temper.

Effect on grain break.—Evidence of an effect of the enzyme on the tightness of grain break is not as positive as it is on drawness and temper. There is an indication, however, that as the enzyme is increased the tightness of break decreases. Five tanneries found this effect either between no enzyme and the regular amount or between regular and ten-fold enzyme, whereas one tannery found no effect on this quality. One tannery found a reversal of this trend in that the control leather was tighter than the zero enzyme test.

Hair cell prominence.—This quality was not evaluated by all tanneries but those that did evaluate it found in general (3 tanneries) that an increase in enzyme produced a flattening of the hair cell, whereas one tannery found no effect.

TABLE II

LEATHER CHARACTERISTICS FOUND IN ENZYME TESTS

(No enzyme [O] vs. normal enzyme [Control] vs. ten-fold enzyme [10 X].)

	Tannery "A"	Tannery "B"	Tannery "C"
Tightness of break	0 = Control Control tighter than 10 X	0 = Control Control = 10 X	0 tighter than Control Control = 10 X
Feel or temper	0 firmer than Control Control = 10 X	0 firmer than Control Control = 10 X	0 firmer than Control Control = 10 X
Drawness	0 more drawn than Control Control = 10 X	0 more drawn than Control Control = 10 X	0 more drawn than Control Control = 10 X
Hair cell prominence	10 X produced open grain appearance compared to others	0 = Control Control = 10 X	Not evaluated
Other evaluations	*Fullness*: Control fuller than 0; Control = 10 X *Veininess*: 10 X showed prominent veins, no difference between 0 and Control *Color*: 10 X lighter and duller than 0 and Control *Uniformity*: 0 less uniform than Control.	*Veininess*: 0 = Control Control = 10 X *Ribbyness*: 0 more ribby than Control; Control = 10 X	*Veininess*: 0 = Control Control = 10X *Ribbyness*: 0 more ribby than control; Control = 10 X

	Tannery "D"	Tannery "E"	Tannery "F"
Tightness of break	0 = Control Control tighter than 10 X	0 tighter than Control Control = 10 X	Control tighter than 0 Control tighter than 10 X
Feel or temper	0 firmer than Control Control firmer than 10 X	0 firmer than Control Control = 10 X	0 = Control Control firmer than 10 X
Drawness	0 more drawn than Control Control = 10 X	0 more drawn than Control Control more drawn than 10 X	0 more drawn than Control Control more drawn than 10 X
Hair cell prominence	Control flatter than 0 10 X flatter than Control	Control flatter than 0 10 X flatter than Control	Not evaluated
Other evaluations	*Color*: 10 X darker than Control and 0 *Physicals*: 10 X and Control slightly higher in Mullen test than 0	*Physicals*: 0 = Control in Mullen test; 10 X stronger than Control in Mullen test	*Crackiness*: 0 more cracky than Control: Control = 10 X *Fine Hair*: 10 X shows less fine hair than Control or 0 *Wrinkles*: 0 more wrinkled than Control or 10 X.

Ribbyness.—Both calf tanneries found that the ribbyness of calf leather was reduced by increase in enzyme up to the regular amount used with no improvement beyond this amount.

Other qualities.—Two tanneries reported that the regular enzyme produced a more uniform leather in temper than the zero enzyme. Two tanneries indicated that the grain strength (Mullen) increased with increasing enzyme, while one tannery found the same trend in terms of double bend crack. One tannery noted that more fine hair was removed by the ten-fold enzyme treatment.

Summary.—From these independent evaluations by six tanneries of the effect of enzyme in the bating process upon final leather qualities, we can draw some fairly rigorous and general conclusions. Increasing the amount of enzyme in the bating process for side and calf leather has the following effects on leather qualities:

1. decreases the drawness (definite),
2. softens the temper (definite),
3. decreases the tightness of break (probable),
4. flattens the hair cells (probable),
5. increases the grain strength (probable),
6. decreases ribbyness in calf (probable),
7. produces a more uniform temper (possible), and
8. decreases fine hair (possible).

These general trends should be of value to all calf and side leather tanners in terms of their own bating processes. The amount of enzyme which will produce any of the effects noted above to a noticeable degree would of course be different for each individual tannery and would have to be determined in terms of each tannery's over-all process. For practical use, however, these trends should enable a tanner to decide which direction to go in terms of amount of enzyme to produce a desired result in terms of leather quality.

The results obtained using ten times the normal enzyme were somewhat surprising in that it was expected that this large amount of enzyme would produce drastic results in the leather qualities. While some effects were noted in the ten-fold enzyme tests they were not anywhere near as drastic as expected. In fact in several of the tanneries the "ten-times" leather was closer in quality to the regular than the "zero" leather. It should be pointed out, however, that in all these tests the amount of delimer was held constant, and therefore the above remarks do not cover the case of using ten times the normal amount of a prepared bate containing delimer.

OTHER BATING VARIABLES

Following this large-scale test in all six tanneries covering the effect of the amount of enzyme, a series of tests was decided upon to measure the effects

of other variables in the bating process. These tests were not carried out by all six tanneries, but from one to three tanneries participated in each test. The experimental procedures and the leather evaluation methods were the same as shown in Table I.

Amount of delimer (two tanneries).—In one test, on calf leather, the ammonium sulfate was varied from ½% to 1½% based on white weight, while the amount of enzyme, time, and temperature were held constant. Over this range of delimer no significant changes were found in the leather qualities of temper, break, ribbyness, or veininess. The trends, although not significant, showed that an increase in delimer might produce a small increase in firmness and a small decrease in ribbyness.

Unfortunately, when this test was run on side leather, both the amount of delimer and the time of deliming were varied in the same test, so that the results do not show the effect of delimer alone. In this case when delimer and time were both adjusted no difference in leather properties was found.

Temperature of bating (one tannery).—A test was conducted at 70°, 80°, 90°, and 100°F. on calfskin using paddle bating. No significant difference was found in drawness, temper, ribbyness, grain smoothness, or grain break at any of the temperature levels. There were indications that the ribbyness might decrease slightly with increase in temperature. Since no real effects were found, this variable was not repeated in another tannery.

Time of bating (2 tanneries).—The effect of time was studied in both calf (paddle bating) and side leather (drum bating). The calf tests were run at ¾, 1½, and 4 hours (normal process, 2 hours); and the side leather tests at ½, 1, and 1½ hours (normal process, 1 hour). The results of these tests were in excellent agreement between the two tanneries in terms of trends and showed that an increase in the time of the bating process produced:

1. a decrease in tightness of grain break,
2. flatter hair cells (side leather),
3. an indication of a small decrease in drawness (both tanneries, but effect small),
4. an increase in firmness (calf only; side showed very small effect),
5. no effect on fine hair or veininess, and
6. an increase in grain strength (Mullen) (side only; calf not evaluated).

Increasing the time of bating, of course, means an increase in time of deliming, time of enzyme action, and amount of mechanical treatment, and these three actions must be considered in comparing these time results with the initial tests of amount of enzyme.

Type of delimer (3 tanneries).—These tests were run to compare ammonium sulfate with ammonium chloride as deliming agents. Two tests were run in

calf tanneries and one in a side leather tannery. In all cases the two delimers were used in chemically equivalent amounts in terms of ammonium ion concentration. These tests showed generally excellent agreement among the three tanneries and indicated that no difference in leather qualities resulted from the use of either delimer.

Water wash before bating.—A test was run in one side leather tannery to determine the effect of the degree of washing the limed stock prior to bating. In the control 4000 gallons were used for 7000 lb. white weight, and for the experiment only 1000 gallons were used. The control pack was bated for 55 minutes to reach the required degree of deliming, whereas it took 110 minutes for the experiment, and even at this point the deliming was not as thorough as the control. However no difference could be found in leather qualities for these two lots. Here both time of bate and amount of wash were varied simultaneously, so we cannot say precisely what the result would have been if the time had been held constant.

Acid wash before bating.—This test was designed to see if either an acid wash, or bating, or both could remove the so-called "lime blast" from stock. Two half packs were held after liming and unhairing with 10 sides from each pack spread out so that some portion of each was exposed to the air for 24 hours. The exposed areas showed drying and discoloration and an indication of carbonate formation either as a patchy white area raised from the grain or as a pebbled grain with pinhead white spots. One pack was given an acid wash treatment followed by lime prior to bating, whereas the other pack was put directly into bate.

The results of this test showed no difference at all between the acid-washed and bated sides and those that were just bated. The leather in the exposed areas was darker in color, empty, tinny, and either cracked or had a tendency to crack whereas the unexposed areas of the same sides were of entirely satisfactory leather quality. Therefore it is evident that lime blast produced by excessive exposure to air of the limed stock is not removed by either acid wash or bating.

Type of enzyme (3 tanneries).—The most commonly used type of commercial enzyme product is one derived from an extract of pancreatic glands adsorbed on wood flour. This type of material has been in general use for many years, and has received full acceptance by most tanners. In addition, commercial enzyme products derived from other sources have been marketed from time to time for bating. These products include bacterial and fungous enzymes, alone or as mixtures with pancreatic enzymes. The manufacturers of these products provide information as to the amount of bacterial or fungous enzyme preparation that is equivalent to their regular pancreatic product. It was decided to test several of these nonpancreatic materials against the

regular pancreatic product at equivalent concentrations (as specified by the bate manufacturer).

The results of these tests are shown in Table III, and we can see some extremely interesting differences between pancreatic and other types of bating materials. The first column in Table III shows a comparison of two pancreatic

TABLE III

COMPARISON OF PANCREATIC BATING MATERIALS WITH BACTERIAL AND FUNGOUS BATES

(All materials compared to pancreatic bates at level recommended by manufacturer.)

	Pancreatic versus Pancreatic	Bacterial Bating Materials versus Pancreatic					Fungous Bates versus Pancreatic		
		Bate A			Bate B	Mixed B plus Pancreatic	Bate C		
	Trostel	Foot	Gallun	Trostel	Gallun	Trostel	Foot	Gallun	Trostel
Tightness of break	Same	Same	Looser	Same	Same	Same	Same	Same	Same
Temper or feel	Same	Same	Same	Same	Same	Same	Slightly softer	Same	Same
Drawness	Same	More	Slightly more	More	Same	Slightly more	Same	Slightly more	Slightly more
Fullness	Same			Slightly less		Same	Less		Less
Ribbyness			Same		Same			Same	
Wrinkles	Same			More		Slightly more			Slightly more
Hair cell prominence			Less smooth		Less smooth			Less smooth	
Crackiness	Same			More		Slightly more			Slightly more

bating materials produced by different companies and used at equivalent concentration, and we see that there are no differences in the leather produced. However, in the case of all the nonpancreatic bates some differences in leather qualities were found, and in every case these differences favored the pancreatic bate. A detailed study of Table III shows that one of the bacterial bates (Bate B) was almost equal in effect to a pancreatic, but that the other bates were no match for pancreatics.

Comparing these data with those for amount of enzyme (Table II), we note an interesting difference. The zero enzyme tests showed that both drawness and temper were effected, whereas the comparison of bacterial and fungous bates with pancreatic showed no differences in temper at all.

In other words these nonpancreatic bates must perform that part of the function of pancreatic bates effecting the softening of the leather but do not possess the ability to reduce drawnness to the same degree.

These results point up the great need for an adequate enzyme evaluation method for tannery bating materials and show conclusively that the present methods used by manufacturers of commercial bates are not satisfactory for assessing enzyme strength for different types of enzymes. Any given evaluation method (such as casein digestion or reduction of gelatin viscosity) is probably adequate for a strength comparison of batches of a given type of enzyme preparation but not for cross comparisons of different types of enzymes. A method has been developed which we feel more adequately meets this need using limed grain layer as the substrate for testing bates. This method was suggested in a previous paper, and further testing of the method will be presented in the near future.

SUMMARY AND CONCLUSIONS

A very comprehensive study of the bating process for side and calf leather has been made in six tanneries with the emphasis being placed entirely on the changes in leather qualities produced. To avoid errors that might be introduced by experimental-sized equipment most of the experimental work was done in full production packs in regular equipment in the tanneries. The organization of the tests was such as to insure adequate controls for each test variable. Evaluation of leather qualities was done in such a way as to prevent bias from affecting the results, and none of the individual tanneries knew of other tanneries' results until all the reports were in.

The results for a six-tannery experiment indicated very close agreement in terms of leather qualities evaluated, such as break, drawness, temper, etc., among the six tanneries (see Table II). In addition, in all the multi-tannery experiments reported in this paper, excellent agreement was also obtained, thus giving the lie to the old adage in the leather industry that what applies to one tannery will not work in another. All our results point in the exactly opposite direction and lead to the conclusion that trends in leather quality established in one tannery will prove to be the same in all other tanneries producing the same kind of leather (even this restriction may not be necessary).

The over-all results for various bating variables are summarized in Table IV, and a study of these should prove valuable both to practical tanners and to chemists who are concerned with side and calf leather. No work has been done on the more thorough bating process usually applied to kidskins, so it is not known whether these results have any bearing on that type of leather. It is apparent from the data that certain bating variables, such as amount and type of enzyme, amount of delimer, and time of bating, have a pronounced effect on leather characteristics, whereas other variables such as type of de-

TABLE IV

SUMMARY OF THE IMPORTANCE OF BATING VARIABLES ON LEATHER CHARACTERISTICS

		Grain Break	Temper	Drawness	Ribbyness	Veininess	Hair Cell	Grain Strength
Amount of enzyme	Zero to 10 X reg.	*	***	***	*	0	*	*
Amount of delimer	½% to 1½%	0	*	0	*	0	?	?
Temperature	70°F.–100°F.	0	0	0	0	?	0	?
Time	About ½ to 1½ normal	***	*?	*	?	0	***	***
Type of delimer	Ammonium sulfate Ammonium chloride	0	0	0	0	0	00	?
Water wash	¼ normal to normal	0	0	0	?	?	0	0
Acid wash	None versus regular	0	0	0	?	?	0	0
Type of enzyme	Pancreatic, bacterial fungous, mixed	0?	0	***	0	?	*	*

0—No effect. ?—Doubtful effect. *—Minor effect. ***—Important effect.

limer and temperature have either a minor, or no, effect over the range investigated. It is also apparent that the conditions of bating definitely affect certain leather characteristics such as drawness, temper, break, and hair cell prominence, but have little effect on ribbyness or veininess of the leather.

This paper has been presented to provide the industry with some much needed basic and objective data relating leather qualities as determined by the tanner to process variables (in this case dealing with bating), and it is hoped that this will stimulate more work of a similar nature in other organizations concerned with leather technology. If the trends in leather qualities associated with changes in various processes normal to leather production could be definitely established by careful, objective, cooperative work, the tanner would be in a much better position to alter the characteristics of his leather to suit the particular demands made upon him both by consumer needs and by sales department desires, in addition to more readily locating production troubles when they occur.

APPENDIX

EVALUATION OF LEATHER QUALITIES FROM EXPERIMENTS IN THE TANNERY

No tannery experiment has value to the tanner unless it can tell him what the effect of the experiment was in terms of leather quality. Since these leather qualities are measured subjectively, some system must be used which

will rule out either accidental or intentional bias. In addition, the method must be fairly sensitive to small leather quality changes, so that trends can be established from a minimum number of experiments and a reasonable number of pieces per experiment. Several workable and apparently reliable systems have been worked out by our group of tanneries and these are explained in detail below.

Subjective scale (good, fair, poor).—This method is the one that has been used for the longest time, and with certain precautions and large enough sample lots it seems to yield reliable information. For this method the selection of stock is highly important, since if the quality and type of stock used varies over wide limits, it is very difficult to interpret the results. The stock selected may be either randomized into an experimental and a control pack, or for greater equalization (with side leather) it may be sided into two packs using alternate right and left sides. In both cases it is necessary that a relatively large lot be taken (full drum load for experiment and control) in order that trends can be seen from the results.

After the leather has reached the point in the process where evaluation is to be done (usually after buffing before finishing, or after finishing), the experimental and control lots should be randomly mixed with each other, renumbered with chalk, and all original identifying marks or punches removed. This step is critical to obtain an unbiased evaluation, since if the sorter can in any way identify each side or skin, he is apt to introduce a bias (perhaps without knowing it) into the results. The evaluation is then carried out by rating each piece on as wide a scale as the sorter can use (very good, good, fair, poor, very poor, etc.) for the particular quality being evaluated. The leather is then re-examined for each other quality in turn. The experimental and control results must then be separated, and these final results examined to determine the differences between the control and experiment. Our group has used a numerical system for this so that the results can be expressed as a numerical average and examined statistically for significance. Of course, the more points on a scale of values that the sorter can retain in his mind, the more sensitive the results, and for this reason a specially trained sorter with considerable experience is required for this type of evaluation.

Matched side method.—This method depends upon the evaluation of the left side against the right side from the same hide where one side has had the experimental treatment and the other, the control treatment. Stock is selected in the green salted condition, and as the hides are sided, the sides are individually stamped for later identification. A system is set up before the siding operation to determine whether a given right or left will go into the experimental or the control pack. This system should provide for a random assignment of lefts and rights; the only restriction being that both experimental and control packs contain the same total number of rights

and lefts. From 20 to 80 matched sides are so identified and assigned, the total number being based upon how small a difference in leather qualities it is desired to find in the final evaluation.

After the sides have been individually stamped, the experimental and control packs are put together and enough unidentified stock of the same general class is added to make up a full production pack. This pack is then run through the regular tannery operation up to the point where the test variable is to be introduced. At this point all the matched sides are removed from the full production pack and further separated into the experimental and control lots. Then sufficient additional unidentified stock (of the same general class) is again added to both the experimental and the control packs to bring them to the weight of full production packs. These two packs are then put through the test and control procedure separately with great care being taken to see that the only variable introduced is the desired test variable.

After the test variable step, the matched sides from both test and control are again sorted out and recombined into a single pack. This pack is then run through the remainder of the regular process steps as a single unit to insure that no differences will occur between the test and control in machine operations, drying, etc.

At the point in the process where the leather is to be evaluated (usually after pasting, after buffing, or after finishing) the matched sides are sorted out of the load and paired up on the sorting table. Then all identifying marks, except the randomized side numbers, are removed, and the sorter begins his evaluation. He is asked to determine whether the right or the left side of a pair is better with respect to a given leather quality. Since he has no way of telling whether the right or left was in the experiment, his judgment cannot be biased. It doesn't matter whether or not he is allowed to call some pairs equal or is required to choose one as better from each pair, since if there is no discernible difference between the test and control, the final result will be a call of roughly fifty percent for the control and fifty percent for the experiment.

After the sorter has evaluated all the pairs for each leather quality in turn, the results are sorted and tabulated in terms of the experimental and control sides. Any tendency for either the experiment or control to be better in a given quality will show up as a majority of the total sides. The greater this majority, the more positive the test results become. This type of data can be handled statistically to establish the significance of the results. This method of evaluation require considerably more time than the previous method but seems more sensitive in picking out small differences in leather quality.

The ranking method.—Another method that has been developed to evaluate whole skins (or sides) depends upon ranking the skins for quality. The same

care and precaution in insuring randomization of stock to experiment and control, and running experimental and control stock together through the tannery except for the test variable step, must be observed as for the other methods.

At the point in the process where the evaluation of the leather qualities is to be made, the test and control skins are thoroughly randomized, all markings removed, and new numbers assigned to each skin. The sorter is then asked to glance through the pack and select one skin which seems to be about average for the particular quality being assessed. This skin then becomes the norm and the sorter goes through all the rest of the pack deciding if each skin is better, worse, or equal to this particular skin. This sorts the leather into three groups. The sorter then takes the best group, again selects one skin as being near the average for this group, and repeats the process. He then evaluates the worst group in the same way. He continues in this fashion until he can no longer tell any differences among the stock in each pile. This over-all process usually results in the separation of the leather into as many as a dozen piles ranging from best to worst for the quality being evaluated.

The sink numbers for each pile are then recorded, separated into control and experiment, and the tendency for either control or experimental skins to predominate at the good or bad end of the scale examined. This can be studied statistically to determine the significance of the results.

This method would seem to be more sensitive than the subjective scale method but requires considerably more time to evaluate. It is probably the best method for proving out small differences between an experimental and control treatment where matched sides cannot be used (as in calf, kid, etc., experiments).

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NHA DIGGING IN HARDER THAN EVER TO BATTLE GRUBS

National Hide Association is carrying its campaign against grubs straight to the rancher and livestock producer. That's where it should help most. Also, NHA will ask the Federal Government to continue to increase appropriations in the budget for grub research and for the eradication of this harmful parasite.

Recent research by the U. S. Department of Agriculture in Washington state showed a reduction in grub infested cattle up to 96% and a reduction in the numbers of grubs up to 98%. In the whole area a voluntary control program over three years reduced the number of grub infested cattle by 85% and grub infestation by 49%.

American National Cattlemen's Association made a recent survey which showed that only 37.7% of the cattlemen are applying any control measures in the fight against grubs.

Why do we continue to tolerate a $100,000,000 plus loss from the insidious cattle grub that scientists long ago proved could be controlled if not exterminated?

— *National Hide Association Bulletin*, April 9, 1957.

A TENTATIVE SIMPLIFIED METHOD FOR THE ANALYSIS OF LIGNINSULFONATES

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ABSTRACT

The ALCA Method for tannin analysis is not suitable for ligninsulfonates because of the slow rate of reaction of the latter with hide powder. An alternative method is described in which the attainment of conditions of equilibrium is greatly hastened. It consists essentially in mixing a portion of specially prepared, air-dry hide powder with a small volume of relatively concentrated sample and after a short absorption period, shaking with a known volume of water and determining the unabsorbed nontannins. Analytical figures are given for a number of ligninsulfonate tanning materials and vegetable tannins. Small variations in the pH of the analytical solution have a marked effect. The method shows promise as a simple and convenient technique for ligninsulfonate analysis.

INTRODUCTION

By definition, tannin is that portion of a tanning agent which combines firmly with hide substance. The official method of the American Leather Chemists Association for tannin analysis (1) is based on this premise, but in the case of ligninsulfonates the method has been shown to be unreliable (2). The results are strongly affected by minor variations in time, temperature, concentration, pH value (3), and surface area (4). The basic cause is the relatively slow rate of reaction of certain fractions of these materials with hide powder and the delay in establishing conditions of equilibrium.

Various modifications have been suggested to induce complete absorption of the ligninsulfonate, chiefly involving increased temperature (5) or prolonged time (6). It has been found, however, that in the case of some ligninsulfonic acid derivatives, and in particular their condensation products with phenol (8), complete uptake is still not achieved. This is particularly true in the case of compounds of high molecular weight.

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Besides the difficulty in obtaining complete absorption, the reaction of the sulfonic acids with the chromed hide powder displaces varying amounts of sulfate from the latter (7). The sulfate appears in the nontannin residue and must be analyzed and corrected for. This correction must itself be corrected because of the sulfate originally present in ligninsulfonates and their derivatives.

The necessity for a rapid and convenient method for tannin analysis arose in the course of our work on the condensation products mentioned above. However, the method which was developed is also satisfactory for ligninsulfonates and, in general, for tanning agents which do not contain insoluble material. A special, highly reactive hide powder, low in water-solubles is required, but the use of this hide powder eliminates the need for chroming and washing, and since no chroming is involved, no correction for sulfate is necessary.

PRELIMINARY EXPERIMENTS

The method which was investigated consisted in mixing the dry, unchromed ALCA hide powder directly with a solution of the tanning agent. Under these conditions it was believed that the reaction between collagen and tannin would be accelerated by the rapid physical absorption of the solution by the dry hide powder. (Dry hide powder has been used previously (9); a chromed, dry hide powder (10) is specified in the filter bell method which is in common use in Europe (11).) In addition, a more concentrated solution than that of the ALCA Method could be used to speed up the reaction still further. Following the mixing of the solution with the hide powder, a known volume of water could be added and the nontannins leached from the mixture. The nontannins could be determined by filtering and evaporating an aliquot of the filtrate to dryness in the usual manner.

It was found that under these conditions the uptake of tannin, although hastened, was not complete. It was also found that the nontannin figures were too high because the hide powder contained more than 1% of water-soluble matter.

Several attempts were made to wash ALCA hide powder free from soluble materials and then dehydrate it with solvents. However, the latter treatment invariably reduced the reactivity of the hide powder. In order to obtain hide powder with a large, freshly cut surface it was decided to prepare it from thoroughly washed, dehydrated pieces of cowhide.

PREPARATION OF HIDE POWDER

A pickled 2-ounce middle split of cowhide is cut into 1-cm. squares and depickled with $NaHCO_3$ and NaCl. It is washed, acidified to pH 4.8 with 1*N*

sulfuric acid, and then washed very thoroughly with running distilled water. The hide pieces are dehydrated with successive changes of acetone until the specific gravity is constant, then with 1:1 acetone-xylene, and finally three times with xylene. The xylene is allowed to evaporate, and the dry hide pieces are ground twice in a Wiley mill with thorough mixing. Hide powder prepared in this way has a large surface area and contains less than 0.2% soluble solids.

ANALYTICAL METHOD

The analytical solution of the tanning material consists of 100 ml. of approximately 2% tan concentration. Total solids are determined on a 15 ml. aliquot.

Into a pint sealer jar, 7.0 g. of hide powder are weighed. Over it are pipetted 15 ml. of the analytical solution as uniformly as possible. The hide powder and solution are quickly mixed into a pasty mass with a thick, blunt-ended stirring rod. The jar is immediately covered and allowed to stand for a total contact time of 30 minutes. During this time the tannin is absorbed by the hide powder. With materials of extremely low reactivity, a longer time and/or a lower tannin concentration may be required.

The pasty mass in the sealer jar is broken up and mixed with 100 ml. of distilled water. The jar is closed again and shaken for 10 minutes to wash the nontannins out of the hide powder. The rest of the method is the same as the ALCA Method and consists of filtering the nontannins solution and determining its solids content. The nontannins filtrate may be tested for the absence of tannin with gelatin-salt reagent. (12).

ANALYSIS OF LIGNINSULFONATES

Some commercial ligninsulfonate tanning agents were analyzed by the ALCA and Ontario Research Foundation methods. The results are given in

TABLE I

ANALYSIS OF LIGNINSULFONATES

	Precipitated Sodium Ligninsulfonate				Ammonium Ligninsulfonate		Fermented Ligninsulfonate	
	From Softwood Cook		From Hardwood Cook					
	ALCA	ORF	ALCA	ORF	ALCA	ORF	ALCA	ORF
Total solids, %	96.2	93.8	96.5	94.3	51.3	49.7	44.7	43.6
Nontans, %	59.4	33.6	59.4	33.1	29.8	22.5	21.1	18.1
Tannin, %	36.7	60.2	37.1	61.2	21.5	27.2	23.6	25.4
Tannin purity	38.1	64.2	38.4	64.9	41.9	54.8	52.8	58.4
pH of analytical solution		3.71		3.78		4.16		2.78

Table I. Gelatin-salt tests for tannin in the nontannins filtrates were positive in the case of the ALCA analyses, and negative for the ORF method. The importance of pH value will be illustrated in a later section.

ANALYSIS OF VEGETABLE TANNINS

The method is not suitable for routine analysis of most vegetable materials because they contain substances which are soluble in hot water but precipitate on cooling. However, it was felt that some comparison with the ALCA Method should be made using vegetable tannins.

Four vegetable tanning materials, two of the catechol type and two of the pyrogallol type, were analyzed by the ALCA and ORF methods. The results are given in Table II. Because of the high tannin concentration (2.7%) of the ORF analytical solution, it was practical to determine only total solids and not soluble solids. As a result, the tannin content could not be calculated by the ORF Method, but the results obtained by the two methods may be compared from the figures for nontannins. When the nontannins are compared on a total solids basis, thus eliminating a slight difference in the total solids determination, agreement is good in the case of myrobalans and chestnut but only fair for quebracho and wattle.

TABLE II

ANALYSIS OF VEGETABLE TANNINS

	Quebracho Solution		Myrobalans Solution		Chestnut Powder		Wattle Solution	
	ALCA	ORF	ALCA	ORF	ALCA	ORF	ALCA	ORF
Total solids, %	28.9	29.1	42.1	41.3	90.4	88.2	6.59	6.46
Soluble solids, %								
received basis	24.5		41.3		88.9		6.53	
total solids basis	84.7		98.1		98.3		99.1	
Nontannins, %								
received basis	2.93	2.8	15.08	14.65	21.6	20.6	1.02	0.92
total solids basis	10.1	9.6	35.7	35.4	23.9	23.3	15.5	14.2

EFFECT OF pH VALUE

The variation in tannin purity with pH value was investigated using two phenol-ligninsulfonic acid condensates (8). Since these condensates contained no insoluble material, the tannin purity was identical with the percentage of tannin on the dry basis. A solution of each condensate was made up, and portions of it were neutralized to different degrees with 1*N* NaOH and analyzed by the ORF Method. Suitable correction in each case was made for the alkali added, so that the results are all on the free-acid basis.

All the nontannin filtrates were colorless, and therefore presumably free from tannin, but these filtrates were not tested with gelatin and salt. The results are shown in Figs. 1 and 2.

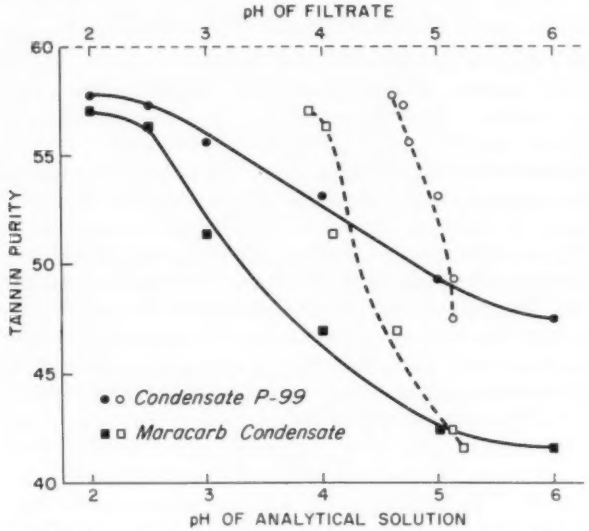

FIGURE 1.—Variation of apparent tannin purity with pH value of analytical solution ——— and with pH value of filtrate - - - - -.

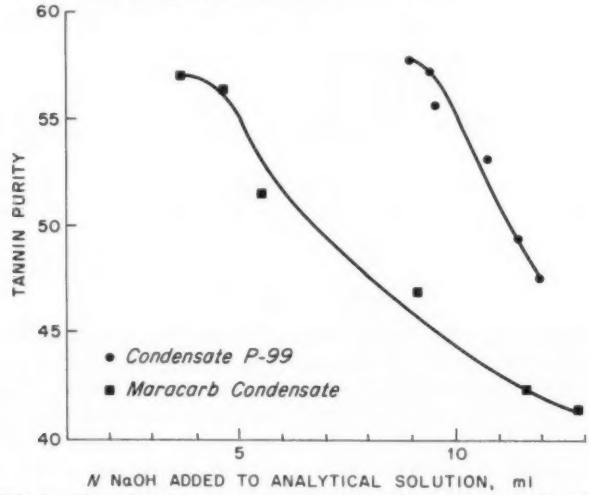

FIGURE 2.—Variation of apparent tannin purity with amount of added NaOH.

The curves follow the general shape of the titration curve of collagen except that they do not fall to zero at pH 5, as is the case with reversibly bound acids. A significant feature of the curves is that a slight change in pH of analytical solution gives a large change in apparent tannin purity. Within the pH range of interest, i.e., pH 3–5, the solid curves in Fig. 1 show least slope at pH 5; therefore it was decided to prepare all analytical solutions of condensates at this pH value. Adjustment of pH may be desirable in the case of ligninsulfonates as well.

FUTURE WORK

In view of the indefinite distinction between tannin and nontannin which is evinced by the effect of pH, some work needs to be done to give meaning to the term "tannin" when used with regard to ligninsulfonates. A laboratory-scale, countercurrent tanning experiment is suggested, more or less in accordance with commercial practice, in which the tanning material entering the system in the feed liquor and leaving the system in the tail liquor and leather would be accounted for quantitatively and a material balance established. A succeeding paper will describe such an experiment, in which the validity of the method described in the present article was confirmed for use on phenol-ligninsulfonic acid condensates.

The investigations reported above were necessarily brief; therefore the effects of varying time, temperature, and concentration under conditions of equilibrium remain to be explored. Certain factors, such as the possible adsorption of ligninsulfonate tannins or nontannins on the filter paper or even on the kaolin, should be examined.

If questions such as these can be answered satisfactorily, the method offers the possibility of completing the tannin analysis of a ligninsulfonate, given forced-air drying equipment, in as little as one day.

ACKNOWLEDGMENTS

The technical assistance of Herman J. Dirschl, Martin Kramer, and Frank W. Clark is gratefully acknowledged. Thanks are due to the Marathon Corporation, Rothschild, Wisconsin; Lignosol Chemicals Ltd., Quebec, P.Q.; and the Robeson Process Co., New York, N. Y. for samples of their products. The condensation products were prepared by John W. Kenny, A. C. Shaw, and Julius Benko.

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MAGIC FOR THE EARLY LEATHER CHEMIST

Wrap an Egg in wax, and with an iron point make letters on it, as far as to the shell; but break it not: for if you break the shell with your iron, or point, or knife, it may be detected. Soak your Egg one night in strong water of depart, which separates gold from silver: in the morning take away the wax, and take off the Egg-shells cover, and hold the shell between your eye and the light, and the letters will be seen very clear quite throughout the transparent shell. The same is done with the juice of Lemmons: for it softeneth the shell; but foul it not, and you shall have your desire.

—From *Natural Magick* by John Baptista Porta, London, 1669, as quoted in *Incunabula of Tannin Chemistry*, M. Nierenstein, London: Edward Arnold & Co., 1932.

As regards the common belief that modern binding leather does decay prematurely . . . while leather of all periods showed some signs of decay, the deterioration becomes more general on books bound after 1830, while some leathers seem to be generally good until about 1860, after which date nearly all leathers seem to get worse. The deterioration of calf bindings at the latter end of the nineteenth century may be attributed as much to the excessive thinness as to the poor quality of the material.

With regard to the conditions under which books are kept, ventilation, lighting, heating, etc., the Committee were satisfied that in libraries where there was no artificial light used, and where the ventilation was good, the bindings were generally in a better state than elsewhere. Where gas is used the bindings are in the worst state noticed, especially on the higher shelves . . . Daylight and still more direct sunlight, has a disintegrating effect on leather.

—From *Some Extracts from the Report of the Committee on Leather for Bookbinding, Appointed by the Council of the Society of Arts*, February, 1900, as quoted in *The Decoration of Leather*, from the French of Georges de Récy by Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

ULTRAVIOLET PHOTOMETRIC METHODS OF TANNIN ESTIMATION IN RELATION TO WATTLE EXTRACT UTILIZATION

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ABSTRACT

The ultraviolet photometric method of tannin estimation, based on an absorption maximum at 280 mμ (1), was recently shown to be highly correlated with the hide powder method for black wattle extracts (2) and was used to investigate the official method (3). An alternative ultraviolet method based on absorption maximum in the far ultraviolet ($\lambda_{max.}$ = 203 mμ) is described, and its relationship with the hide powder and existing photometric procedures ($\lambda_{max.}$ = 280 mμ) is assessed. Attention is drawn to the accuracy and applicability of photometric methods as elegant research tools and rapid estimation methods in leather chemistry.

INTRODUCTION

Photometric methods of analysis have been used increasingly in recent years for the estimation of a wide variety of organic and inorganic substances. This is evidenced by the increased proportion of photometric procedures published in almost all journals of analytical chemistry. It is due partly to improved instrumentation but also the development of the differential method (4), by which superior accuracy may be achieved in almost all instances compared with alternative volumetric and gravimetric procedures.

In the field of leather chemistry there is wide scope for these new, more rapid, and elegant procedures. Leather chemists, however, even today tend to lean heavily on their accumulated tradition in analytical technique and are relatively slow in developing, accepting, and introducing more progressive methods of analysis. In fact, once an analytical method has received the official sanction of any group of leather chemists, that method tends to remain firmly entrenched in spite of the fact that it may possibly be empirical in nature and the factor measured unrelated to practical usage in certain instances.

To this class belongs the hide powder method of tannin estimation, which is open to much criticism (3). For example, "tannin" values derived by this method are largely arbitrary, as the conditions of estimation employed, however reproducible, have not thus far been related to those of commercial usage. The empirical nature of the hide powder method is reflected in the variable conditions of estimation used, and in that those procedures (shake and filter bell methods) which have gained local recognition in certain parts of the world give results differing by as much as 5–7% on identical natural extracts (5).

The hide powder shake method, while obviously reflecting a wholly arbitrary "tannin" value for gambier extract, does not furnish a satisfactory criterion of extract quality, as the *d*-catechin of which the phenolic fraction of the extract is almost wholly composed, "tans" hide powder under official conditions to the extent of 64% (6). Other extracts rich in flavonoid compounds will be affected in the same way, e.g., pine bark extract (7). This has to be related to the case of wattle extract, where a low percentage of known flavonoids appear to be quantitatively absorbed by the hide during tannage (8).

Roux (3) recently showed that the alcohol-insoluble fraction of wattle extract, consisting mainly of natural hydrocolloid gums, is reflected as "tannins" by the shake method, although the penetration of these gums into hide or skin may be limited by their large molecular size. This fact, as well as others, has led the author to the conclusion that the evaluation of each extract in relation to extract utilization is essential before the "tannin" content may be approximately assessed.

The value of the author's ultraviolet photometric method ($\lambda_{max.} = 280$ mμ) of estimation (1) has been demonstrated on a statistical (2) and analytical basis (3) for black wattle tannins, and the application of this method for investigating the hide powder method has been illustrated (3). Onikienko (9) recently described this as a "new" method, and showed close agreement between spectrophotometric and hide powder methods for tannins from *Aspidosperma*, willows, *Spiraea filipendula*, and oak. The general application of the ultraviolet method as an analytical tool and as a method of tannin estimation, therefore, appears feasible.

NEW ULTRAVIOLET METHOD

To the U.V. method previously used ($\lambda_{max.} = 280$ mμ) may be added a second one of even greater sensitivity. As in the case of tea tannins (10), wattle polyphenols exhibit a second and exceptionally intense absorption maximum at 202–203 mμ (Fig. 1). This absorption peak in the far ultraviolet exhibits an absorption density approximately 15.9 times as great as that at $\lambda_{max.} = 280$ mμ for the same black wattle tannin solution. Measurement at the lower wave length peak has the advantage of extreme sen-

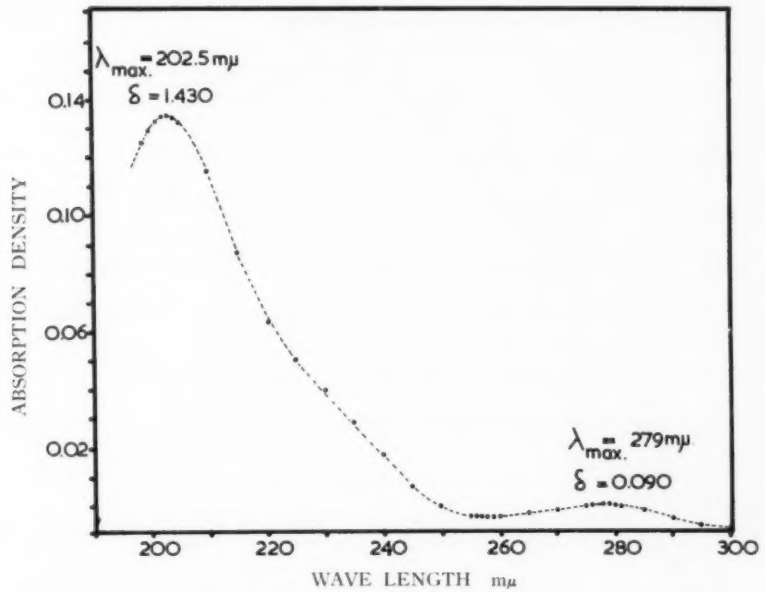

FIGURE 1.—Absorption density of wattle solution at different wave lengths (Unicam S. P. 500 spectrophotometer).

sitivity but also the disadvantage that larger volumes of water are required for dilution, coupled with the use of smaller weights of extract, in order to obtain the same range of readings on the spectrophotometer.

The absorption maximum at 202–203 mμ for wattle tannins is close to the lowest wave length reading normally attainable (199 mμ) on the Unicam Model S.P. 500 spectrophotometer when using water as solvent. The question now arises as to whether this peak is real or a spurious one resulting from measurement close to the extreme of which the instrument is capable. To answer this question an automatic recording Beckman Model DK-1 was employed capable of measurement down to 190 mμ. Wattle extract solutions examined at different concentrations (Fig. 2) showed that the absorption maximum at 202–203 mμ was real.

With this fact established, the analytical standard curve was prepared at 203 mμ, with water as cell blank using the Unicam SP-500 spectrophotometer. Due to the extreme sensitivity of the method, and in order to avoid working with unduly copious volumes of water, the amount of extract weighed was considerably reduced compared with usual analytical solutions. 0.2, 0.4, 0.6, and 0.8 g. quantities of powdered analyzed extract (62.6 and 62.7%

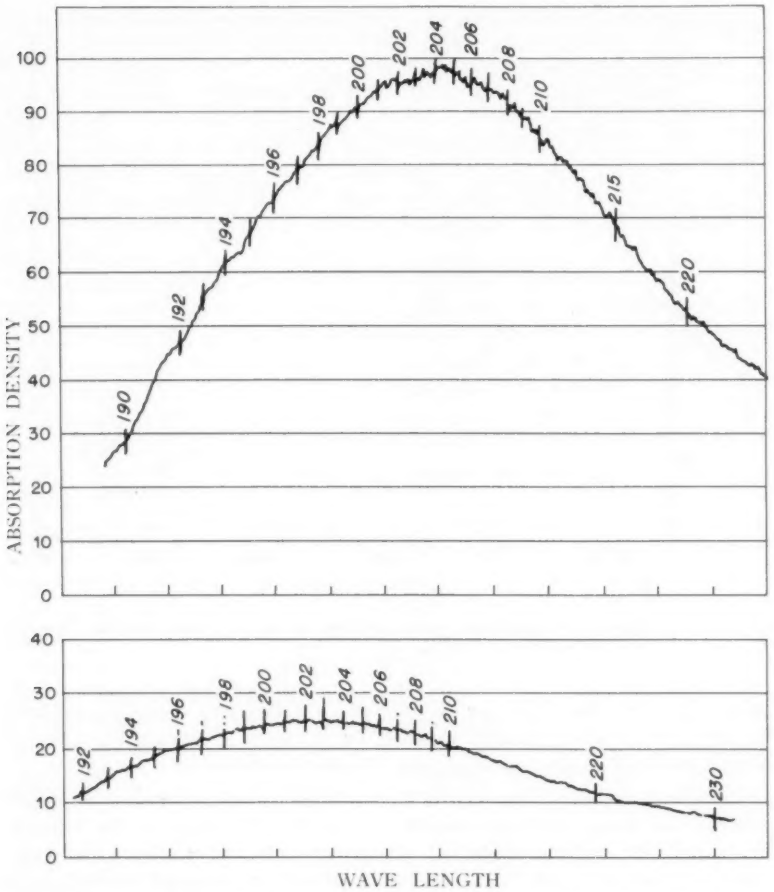

FIGURE 2.—Absorption densities of two wattle solutions at wave lengths near 203 mμ. (Beckman DK-1 spectrophotometer).

tannins by hide powder and ultra violet (280 mμ) methods respectively) were dissolved in 500 ml. hot water (above 60°C.), slowly cooled, and finally diluted to one liter. These solutions were further diluted 100-fold (10 ml/l or 5 ml/500 ml), and the absorption density of each was measured at 203 mμ. Cell blank corrections were made and rechecked after each measurement. Table I and Fig. 3 show that the Beer's Law relationship is obeyed also in this instance. Inaccuracies due to lack of homogeneity in the small quantity of extract weighed in each instance appear to be small.

TABLE I

STANDARD CURVE FOR WATTLE EXTRACT (62.7% TANNINS)

(*Working conditions: slit width* = 1.9 *mm.* 203 *mμ.*)

Grams Extract Per Liter	δ
0.2006	0.267
0.4009	0.521
0.6016	0.781
0.7998	1.034

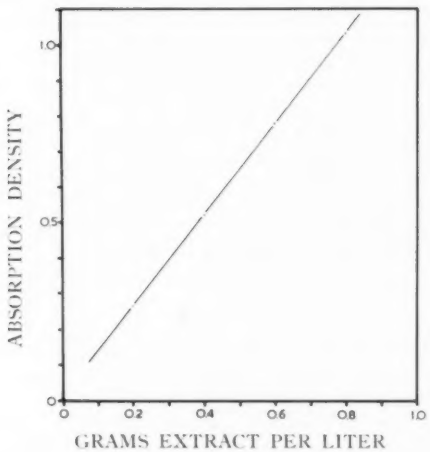

FIGURE 3.—Relation between concentration of wattle solution and absorption density at 203 mμ.

For solid extracts of unknown tannin content, about 0.4 g. powdered extract was weighed accurately, dissolved as before, and made to one liter. Further careful 100-fold dilution preceded measurement in the spectrophotometer at 203 mμ. Cell blank values were examined after each measurement, and the appropriate correction was applied. Tables II–IV compare batch analyses of commercial black wattle extracts by (*a*) the hide powder method, (*b*) the 280 mμ U.V. method, and (*c*) the 203 mμ U.V. method.

DISCUSSION

Tables II and IV show the high degree of concordance between spectrophotometric measurements at 203 mμ and the hide powder method, and also

between the two ultraviolet methods using different instruments. The standard curves for the 203 mμ and 280 mμ methods were obtained by using extracts analyzed by different analysts.

TABLE II

SPECTROPHOTOMETER AT 203 mμ VS. HIDE POWDER

Sample No.	% Tannins		Difference
	Hide Powder	Spectrophotometer*	
214A	60.8	62.9	+2.1
218A	61.0	63.2	+2.2
219A	62.6	63.0	+0.4
300B	60.2	59.7	−0.5
303B	62.0	60.0	−2.0
304B	61.9	62.6	+0.7
305B	63.5	63.3	−0.2
298	60.9	59.5	−1.4
301	61.7	61.8	+0.1
302	62.6	63.2	+0.6
303	62.2	63.2	+1.0

*Measurements made with a Unicam SP-500 Spectrophotometer.

TABLE III

SPECTROPHOTOMETER AT 280 mμ VS. HIDE POWDER

Sample No.	% Tannins		Difference
	Hide Powder	Spectrophotometer*	
214A	60.8	61.9	+1.1
218A	61.0	62.3	+1.3
219A	62.6	62.7	+0.1
300B	60.2	61.4	+1.2
303B	62.0	60.9	−1.1
304B	61.9	62.8	+0.9
305B	63.5	63.0	−0.5
298	60.9	61.4	+0.5
301	61.7	62.0	+0.3
302	62.6	62.8	+0.2
303	62.2	62.9	+0.7

*Measurements made with a Beckman Model DU Spectrophotometer.

Statistical methods were used to assess the significance of the comparison of the various methods (11). First the *t*-test was employed to show whether the methods differ significantly in the average of their results, using the

difference method in order to eliminate differences between samples. From Table V it is clear that it could not be shown statistically that the averages of the results by the various methods differ significantly.

TABLE IV

SPECTROPHOTOMETER AT 280 mμ VS. 203 mμ

Sample No.	% Tannins		Difference
	Spectrophotometer*	Spectrophotometer†	
214A	61.9	62.9	+1.0
218A	62.3	63.2	+0.9
219A	62.7	63.0	+0.3
300B	61.4	59.7	−1.7
303B	60.9	60.0	−0.9
304B	62.8	62.6	−0.2
305B	63.0	63.3	+0.3
298	61.4	59.5	−1.9
301	62.0	61.8	−0.2
302	62.8	63.2	+0.4
303	62.9	63.2	+0.3

*Measurement with a Beckman Model DU Spectrometer at 280 mμ.
†Measurement with a Unicam SP-500 Spectrophotometer at 203 mμ.

TABLE V

t-TEST AND ITS SIGNIFICANCE

Comparison	t	ϕ	Significance
Hidepowder and 203 mμ	0.697	10	not significant
Hidepowder and 280 mμ	1.91*	10	not significant
203 mμ and 280 mμ	0.529	10	not significant

*For 10 degrees of freedom the 10% probability level is 1.81 and the 5% point is 2.23.

The F-test, or variance ratio, was used to establish whether the two sets of data show significantly different degrees of spread (Table VI).

This variance ratio unfortunately also includes the known differences in value between samples. In spite of this, the comparison of hide powder with both ultraviolet methods cannot be shown to possess significantly different degrees of spread. Comparing the two U.V. methods, however, a much larger and significant F value is obtained, which suggests interaction between sample and method. By inspection and comparison of the difference columns in Tables II and III it will be found that, with the exception of samples 300B

and 298, the differences relative to the hide powder values are in the same direction for each sample with both U.V. methods, the magnitude of difference being greater for the 203 mμ method in most instances. This greater degree of spread is probably reflected in the high F value.

TABLE VI

F-TEST AND ITS SIGNIFICANCE

Comparison	F	Significance
H. P. vs. 203 mμ U. V.	2.53	Not significant at 10% level
H. P. vs. 280 mμ U. V.	1.80	Not significant at 10% level
280 mμ U. V. vs. 203 mμ U. V.	4.55	Significant at 10% (2.98) and very nearly significant at 2% level (4.85).

Calculation of the correlation coefficients between the various methods (Table VII) showed highly significant correlation between the two photometric methods. Correlation was less significant for the 280 mμ U.V. method and least significant for the 203 mμ U.V. method compared with the hide powder method.

TABLE VII

CORRELATION COEFFICIENTS

Comparison	Correlation Coefficient	Level of Significance*
H. P. vs. 203 mμ U. V.	0.550	Significant at 10% level but not at 5%
H. P. vs. 280 mμ U. V.	0.652	Significant at 5% level but not at 2%
203 mμ U. V. vs. 280 mμ U. V.	0.880	Significant at 0.1% level

*For 9 degrees of freedom the 10%, 5%, 2%, 1% and 0.1% levels of significance are 0.521, 0.602, 0.685, 0.735 and 0.847 respectively.

With the number of samples taken, therefore, it cannot be shown that the photometric and hide powder methods differ significantly in the average of their results or have significantly different degrees of spread. The two ultraviolet methods again appear to be exceptionally highly correlated, but measurement at 203 mμ gives a higher degree of spread of results.

Todd (10) has shown that the U.V. absorption spectrum for tea polyphenols (gallocatechins, catechins, and their gallates) is identical with that of the extract of the tea leaf ($\lambda_{max.}$ = 270 mμ and 205 mμ) and that the polyphenols are responsible for the strong absorption at $\lambda_{max.}$ = 205 mμ. Furthermore,

the absorption density and the polyphenolic content (oxidizable matter) fall as the fermentation proceeds and the values of the two show highly significant correlation during the process.

For wattle tannins the adsorption at 203 mμ is also significantly correlated with the "tannin" content reflected by the hide powder method (this has also been shown for $\lambda_{max.}$ at 280 mμ [2]), although the hide powder method allows the escape of some phenolic material and partly estimates certain nonphenolic extract components, e.g., hydrocolloids, as "tannins" (3). For wattle tannins the adsorption at 203 mμ appears to be due to the phenolic content and has the advantage that extract solutions in corked measuring flasks show no increase in adsorption maximum during overnight storage at this wave length. By comparison, use of the alternative U.V. method (280 mμ) requires the addition of traces of reducing agents (1) or else simple pH adjustment (12) to stabilize the solution against atmospheric oxidation. Atmospheric oxidation tends to cause increases in adsorption density at 280 mμ.

For the 280 mμ U.V. method it has been established that substantial pH variation on the acid side (pH 1.95 – 4.80) does not affect adsorption density readings on the spectrophotometer:

Analytical solution (10 ml.) diluted to 1 l. with:	Absorption density (cell-blank corrected)	pH
0.1 *N* HCl	0.545, 0.544	1.95
0.01 *N* HCl	0.541, 0.541	2.25
0.001 *N* HCl	0.551, 0.551	2.75
0.3% $Na_2S_2O_8$	0.542, 0.542	4.80

Should solutions, however, be made alkaline, substantial alteration in the adsorption density will result (13), accompanied by undesirable oxidation effects. It is perhaps a weakness also of the hide powder method that no pH specification is included in the official procedure. Estimation by the hide powder method obviously cannot be performed with alkaline tannin solutions, and all methods will thus be affected by alkaline conditions. Nayudamma's criticism (14) of the U.V. method by pointing out the dependence of adsorption on pH, while correct in part, does not appear justified for the acid range (at the natural pH of the extract) in which U.V. adsorption measurements normally are made.

The facts that tannin content is measurable at two adsorption maxima, 280 mμ, and 203 mμ, and that the latter method is largely unaffected by the darkening of extract solution and thus useful for following the destruction of tannins by enzymic action, are important factors in the choice of photometric apparatus. The far ultraviolet range (199–220 mμ) is not covered by all instruments, e. g., Beckman Model DU.

CONCLUSION

Both ultraviolet methods and also the ferrous tartrate colorimetric method (1) of estimating black wattle tannins are of inestimable value as research tools in tannin and tanning chemistry. For example, they may be used:

a) For controlling the polyphenolic content of extracts during manufacture as compared with the "tannin" content by the hide powder method. Differences between these, if reproducible, may give some indication of abnormal nonphenolic hydrocolloid concentration in the extract (3). Thus, for wattle extract, it may be used, for example, in furthering the homogeneity of an exceptionally uniform product.

b) For estimating the percentage residual polyphenolic material in spent bark after commercial extraction. Much of the soluble material left is of a carbohydrate hydrocolloid nature and is capable of "tanning" hide powder. Inclusion of this fraction in the extract is undesirable, while at the same time the economic extraction of polyphenols is aimed at during manufacture. The colorimetric methods are therefore of obvious value in assessing residual polyphenols.

c) For examining (ultraviolet methods only) the adsorption of polyphenolic tannins by hide during tannage, and for furnishing a truer index of the "tannins" content in spent liquors, where gums capable of "tanning" hide powder and affecting barkometer values normally tend to accumulate.

d) For studying the composition of sludges likely to contain both phenolic and nonphenolic extract constituents. This, in addition to the analysis of completely spent liquors, should assist considerably in assessing tanning losses in relation to extract consumption.

e) For the estimation of the percentage desorption of phenolic tannins from leather as a fraction of the total desorbed extract.

f) For studying the desorption rate of polyphenols from various leathers.

In the light of the above, the author confidently predicts a wide use for these rapid photometric methods, both as research tools and also for the estimation of tannins in a wide variety of barks and extracts.

ACKNOWLEDGMENT

Thanks are due to Mr. Z. J. Kimmerling, Hodgson's Extract Co., Merebank, Natal, for supplying analyzed extract samples and for assistance in some of the ultraviolet analyses; to the Council of Scientific and Industrial Research, Pretoria, for permitting the use of the Unicam S. P. 500 and Beckman DK-1 spectrophotometers; to Mr. L. M. Hill of this Institute for dis-

cussion regarding statistical analyses; and to Miss C. Pike for assistance in their calculation.

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ON BOOKBINDING LEATHER

We are of opinion that no special skin can be condemned in its original condition, although goat, seal, pig, and calf are probably superior in strength of texture to sheep. Sheepskins are, however, equally resistant to chemical agencies, and being naturally soft and flexible, are extremely suitable for use for purposes where they are not much exposed to mechanical wear.

Fresh market skins, dry skins, or wet salted skins are much to be preferred to those known as "dry-salted", since the crystallization of the salt which takes place in the drysalting process, tends to weaken the structural fibre of the pelt. No tainted or putrefied skins, even if only slightly affected, are suitable for the manufacture of bookbinding leather, both for the same reason, and because the weakness of grain so produced leads to uneven dyeing.

In the soaking of skins we would strongly condemn the use of old putrid soaks, or the addition of salt to the soaks to assist in the softening, as both methods weaken the skin . . . Violent mechanical treatment such as "stocking" is injurious.

Pure sumach is the tannage we would most strongly recommend for high class bookbinding.

—From *Some Extracts from the Report of the Committee on Leather for Bookbinding, Appointed by the Council of the Society of Arts*, February, 1900, as quoted in *The Decoration of Leather*, from the French of Georges de Récy by Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

PAPER CHROMATOGRAPHIC ANALYSIS OF THE NAPHTHENIC SYNTANS

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ABSTRACT

Conditions for chromatographic examination of naphthalene syntans have been studied, including choice of paper, solvent phase, and developing agent. Basic dyes, particularly Methyl Violet 2B, are suitable developing agents. Examples of chromatograms of commercial syntans are given, and a possible application of the chromatographic procedure is suggested.

—×—×—

INTRODUCTION

We all know that paper chromatography is one of the most efficient methods for the qualitative and quantitative investigation of compounds in general. We can also use it as an improved control during fabrication, thereby easily distinguishing the different impurities which may appear in secondary reactions. Using paper chromatography in the investigation of syntans, we have succeeded in obtaining very favorable results (1), and as a consequence we believe that this technique presents a quite easy manner of controlling the fabrication and use of these compounds.

Our greatest difficulty was to obtain a simple and easy reaction capable of staining these derivatives with precision; it was only after we had succeeded in this that we were able to use paper chromatography and apply it to the important compounds which are employed in tanneries. Among all known syntans the naphthalenes are those which show a rather reduced reactivity with most of the chemical reagents used in the normal colorimetric test of these compounds. Since naphthalenic syntans form almost no colored compounds, contrary to what happens with phenolic derivatives, we had to look for a reagent capable of revealing their chromatographic maps with facility. This became possible through the use of basic dyes. As a result of several tests regarding the development of the chromatographic maps and covering a rather extensive number of naphthalenic syntans, we consider this method to be fully satisfactory.

PROCEDURE

For our tests, we have used filter paper (30 x 30 cm.) cut as shown in Fig. 1 (I). The advantage of paper cut in this manner over the other types of cylinder formation is that its vertical edges are not united and the cylinder

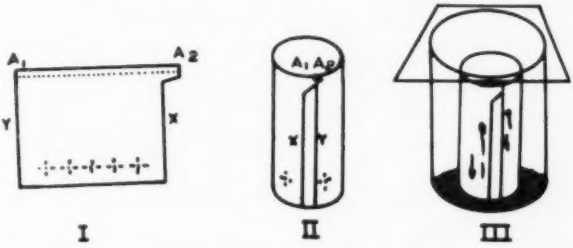

FIGURE 1.—Arrangement of paper for chromatography.

always remains vertical without needing any fixation system along these edges. The stability of the cylinder is ensured through the filter paper belt A_1–A_2, which is obtained by folding along the dotted line seen in Fig. 1. This part, which may be turned either inward or outward, keeps the cylinder firmly in position; a paper clip is put on the A_2–A_1 belt for greater safety, and in such a way that it does not touch the edge x or y, the position of which is illustrated in Fig. 1 (II).

With the paper cut as explained above, one should mark the respective starting points of the compounds which are to be chromatographed. The syntan (5% solution in water) is put in this position by means of a micropipet or capillary tube, allowing the solution to spread until a spot of a maximum of 2 mm. in diameter is obtained. Allow sufficient time for the spot to dry, form the cylinder, and put it into a chamber which already contains the solvent (Fig. 1 [III]). Cover well, using lanolin, vaseline, or paraffin to insure complete sealing. Allow some time for development. This part is concluded when the solvent covers some 90% of the paper. Take out the cylinder, open borders A_2 A_1, and allow to dry entirely.

Among the stainers tested by us, Methyl Violet 2B (C. I. 680) was the one showing the most adequate characteristics, as will be shown later. The development solution is prepared by dissolving 0.5 g. of the dye powder in alcohol. Alcohol was used as solvent because sulfonated compounds (syntans) are not soluble in it and consequently are not removed from the paper. The staining solution is placed in a tray larger than the paper, and the developed paper is immersed completely for 5 to 10 minutes. The paper is then transferred to a second tray containing distilled water to wash away the excess dye. This rinsing operation is repeated as many times as necessary to obtain a lilac-tinted background to the violet spots. The paper is then blotted

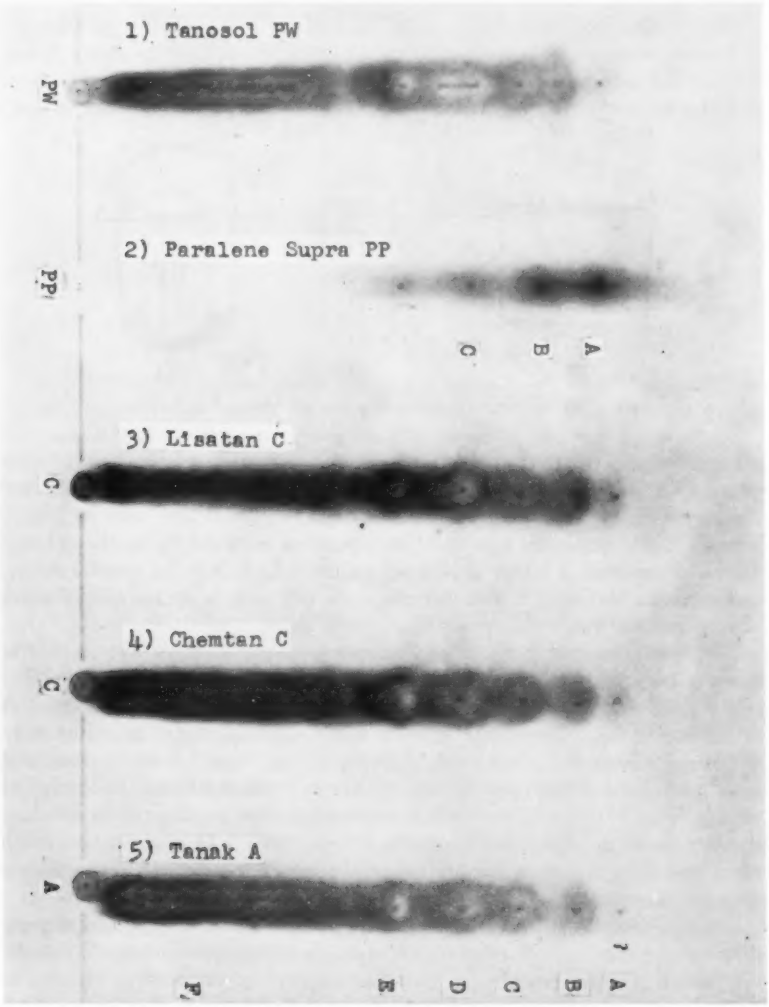

FIGURE 2.—Chromatographs of commercial naphthalene syntans.

between two pieces of white blotting paper and dried, preferably in a horizontal position and not on the blotting paper.

The spots in a chromatogram are characterized by their Rf values, Rf being the ratio of the distance between the starting point and the point of

greatest density of the spot to the distance between the starting point and the solvent front. Small differences between some Rf values may be attributed to differences in concentration of the syntan (see Figure 2). The Rf value for any component is constant only for a given set of conditions. Any change in conditions (paper, solvent, temperature, or relative humidity in the chromatographic chamber) will change the Rf values, so that it is always necessary to perform these tests under standardized conditions in order that results may be comparable.

Figure 2 illustrates the type of chromatogram obtained by this procedure with five different commercial syntans of the naphthalene type. This chromatogram demonstrates clearly that all these products are very similar in composition.

Having set forth our general procedure, we shall now discuss the experimental work that was done to arrive at the most favorable conditions.

CHOICE OF DEVELOPMENT AGENT

In choosing a developing agent, we started from the premise that syntans react readily with basic dyes, forming insoluble compounds of definite color which show well on the paper, while alpha cellulose has a rather restricted affinity for basic dyes. Taking advantage of these facts, we have obtained chromatographic maps that are easily identified. It was necessary to choose a dye that forms a lake that is not dissolved when the excess dye is washed out of the paper. Thus, when we used Malachite Green (C. I. 657) or Auramine O (C. I. 655), we found that the lake was partly dissolved by the washing. On the other hand, Methyl Violet (C. I. 680) formed a very insoluble lake, and the excess dye was easily removed from the paper, leaving a pale blue or violet background. Similar results were obtained with Rhodamine B (C. I. 749). Safranine T (C. I. 841) proved to have too much affinity for the paper, so that the dye was but slightly removed from the paper by washing.

TYPE OF PAPER

Filter papers differ with respect to retention capacity, ash content, etc., and it is possible to find a logical relationship between retention and the duration of chromatographic development. Papers whose retention is limited give a slow development, and vice versa, with the production of different chromatographic maps. The differences in three papers selected for study are summarized in Table I. The value *D* is the ratio of solvent phase height in centimeters to time of travel. The greater the value of *D*, the faster the paper, and consequently the less detail that will be obtained in the chromatogram. The value of *D* is more or less related to the capillarity of the paper. The values for *D* given in Table I apply only to the solvent system that we employed (8 butanol : 2 ethanol : 4 formic acid : 5 water). These values are

valid only for distances exceeding 15 cm. ascension of the liquid phase. Factors influencing the rate of ascension include the kind of solvent, its viscosity, and pH; the kind of paper, its capillarity and pH; and the degree of saturation of the chamber atmosphere with solvent vapor.

TABLE I

COMPARISON OF SCHLEICHER & SCHULL PAPERS

No.	Surface	Weight g/m²	Thickness mm.	Capillarity	D*
2040a	rough	90 – 95	0.18–0.19	100/110	4.92
2043a	rough	90 – 95	0.18–0.19	90/95	3.60
2045aGl	smooth	90 – 95	0.10–0.11	60/70	3.40

* D—Phase height in cm. / time

The S. & S. No. 2043a paper was adopted as the standard.

SOLVENT PHASE

In order that the solvent phase may work satisfactorily, it must possess a certain solvent action on the compounds being chromatographed, and there must exist a certain ratio between the affinity of the chromatographed substances for the solvent and for the paper, thus resulting in a distribution of the substance between the two phases, solvent and paper. The role of the paper is not simply that of a support for the solvent. The hydroxyl groups of cellulose make possible the formation of compounds with the substance, and it is the ratio of the polarities of solvent and cellulose that determines the development of the chromatogram (2).

Since syntans do not possess a very marked affinity toward cellulose, they may easily be pulled along the paper. But since they are also highly dissociated compounds, their chromatographic investigation becomes more difficult; there always takes place the formation of bands, tails, etc., which are rather pronounced. Due to this, we must always use a solvent phase where this dissociation is very small.

We have tested a great number of phases—acid, neutral, or alkaline—but unfortunately it has not been possible to eliminate entirely the formation of these tails. Our best results were obtained with the butanol : ethanol : formic acid : water (8:2:4:5) phase. This mixture, however, presents the grave inconvenience of not being sufficiently stable, being suitable only for immediate usage, since we have observed that it becomes entirely decomposed after 48 hours and gives completely different chromatograms from those initially obtained.

APPLICATION OF CHROMATOGRAPHIC ANALYSIS OF SYNTANS

The manufacture of naphthalene syntans usually involves two steps: first, the sulfonation of naphthalene, and second, the condensation of the sulfonated molecules by means of formaldehyde. During the sulfonation, both the alpha- and beta-sulfonic acid may be formed—the latter predominating at higher temperatures. During the condensation, compounds of differing degrees of polymerization will be formed, as has been shown by Schütte (3) for the condensation of p-cresolsulfonic acid with formaldehyde. Both the alpha-beta isomerism and the degree of polymerization may be expected to influence the chromatogram yielded by the syntan.

SUMMARY

A procedure for examining naphthalene syntans by paper chromatography has been developed in which basic dyes are used to reveal the chromatographic spots. Studies have been made to determine the most suitable paper, solvent mixture, and basic dye. Application of the procedure to commercial naphthalene syntans reveals that all those tested had essentially the same composition.

The procedure is well adapted for use as a rapid control method during the manufacture of syntans and should be useful in detecting the presence of different isomers and components of differing degrees of polymerization.

ACKNOWLEDGMENT

We take this opportunity to express our thanks to all those who furnished us material for these tests, and especially to the Brazilian and foreign companies which have given us their collaboration.

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The introduction of decorated leather for hangings and furniture into Spain may be attributed to the Moorish conquerors about the eighth century. In an Arabian manuscript of the sixth century of the Mohammedan era, mention is made of the industry as flourishing in the town of Ghadames in the Sahara. Jehan de Garlande, author of a Latin dictionary composed in 1080, mentions *Cordouans* first manufactured at Cordova in the eleventh century. About the same time, the Monk Theophilus, in his curious encyclopedia of the arts which unfortunately has not come down to us in its complete form, gives a description of the processes of gilding leather.

—*The Decoration of Leather*, from the French of Georges de Récy by Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

LIFE LINES

Brief Biographies of Our Contributors

W. R. KENZIE is an honors graduate in chemistry from the University of Toronto. He joined the Ontario Research Foundation staff in 1950 to work on leather specifications for the Canadian government. He has been associated with the Foundation's project on tanning agents from lignin and has published papers on this subject in this *Journal*. At present he supervises leather and tanning research at the Foundation.

P. A. DEUTSCH is a graduate of the University of St. Andrews. He has worked in the fields of dyes and cosmetics as well as leather and is now engaged in the development of protective coatings.

DR. D. G. ROUX.—See the February, 1957, issue of *JALCA*.

DR. ROBERT STUBBINGS.—See the October, 1956, issue of *JALCA*.

In considering the many problems involved in attaining the objective of developing more and better qualified scientists and engineers, three basic considerations must be kept in mind:

First, the number of youth of college age is now at low ebb—about one million lower than in 1940. This number will rise gradually until 1960 after which the number will move rapidly toward a new high level.

Second, increasing the supply of qualified scientists and engineers is only one part of the larger problem of increasing the supply of highly qualified college graduates in all fields. For various reasons, only about a third of the young people graduating from high school enter college on a full time basis and less than a fifth of the high school graduates attain the bachelor's degree, the minimum level of education required for qualified engineers. Less than 2 percent of those judged to be mentally capable of studies at the doctorate level obtain the Ph.D. degree or its equivalent, the level of education required for highly qualified scientists. If with proper motivation and opportunity a substantially larger proportion of qualified youth pursued training toward a degree, the normal selective pattern would provide a greatly increased continuing supply of trained scientists and engineers.

Third, increasing the supply of qualified scientists and engineers is impeded by the need for a general improvement of staff and facilities of secondary schools. Without obtaining additional qualified mathematics and science teachers at the secondary school level, we cannot take care of foreseeable growth. This problem will become more grave because the school age population growth is at present considerably greater than the increase in facilities.

Despite these very real obstacles, the picture is not all dark. College enrollments show that the freshman classes in engineering have been increasing rapidly during the past three years, and this increase will continue. On the long-time pull, enrollments in engineering will participate in the general increase in college enrollment between 1965-70, and there is reason to hope that the same increase might be reflected in the field of science.

Nevertheless, expanding technology and an expanding economy are producing demands for highly qualified scientists and engineers beyond the numbers who are preparing themselves for this work. It is not enough to plan for presently estimated needs; it is expected that the demand for trained scientists and engineers will accelerate as new discoveries open up areas for further exploration and application. Again, while increasing the number is important, the immediate need is to upgrade the quality of both scientists and engineers.

—The National Committee for the Development of Scientists and Engineers, *The General Problem*. Washington D. C.: National Science Foundation, 1956.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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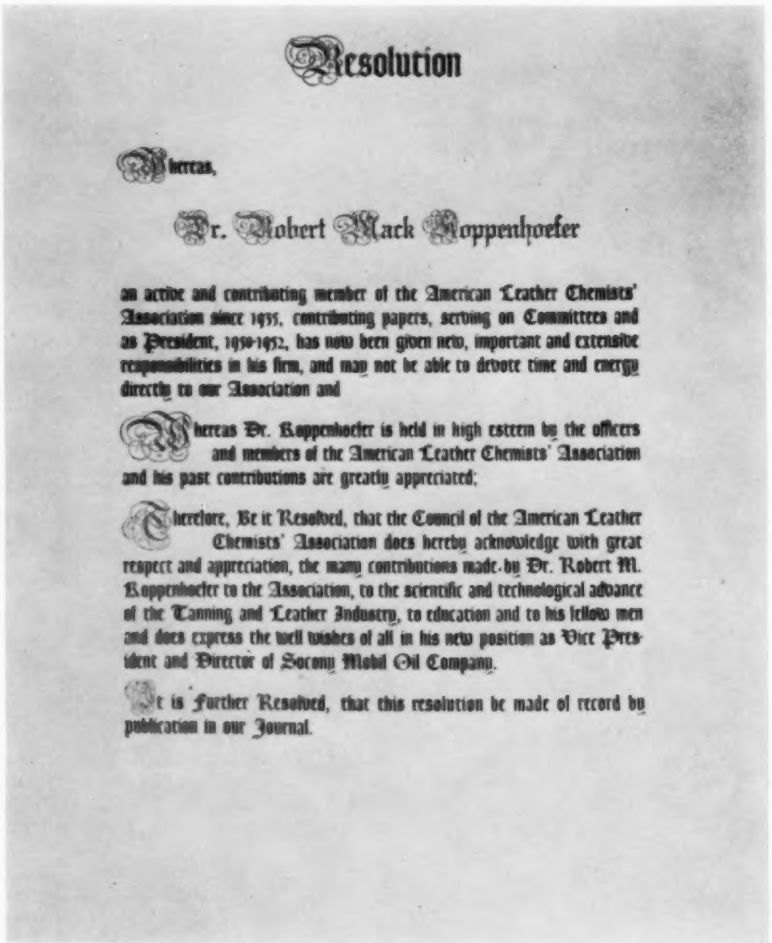
CHANGE IN I.U.L.C.S. PROGRAM

Because of the number of papers submitted, the Fifth Congress of the International Union of Leather Chemists' Societies, which opens in Rome on September 15, 1957, will last one day longer than previously announced. Friday, September 20, will be devoted to the reading and discussion of papers and reports of international commissions. The audience with His Holiness the Pope, previously scheduled for Friday, will take place on Saturday, September 21.



Resolution

Whereas,

Dr. Robert Mack Koppenhoefer

an active and contributing member of the American Leather Chemists' Association since 1935, contributing papers, serving on Committees and as President, 1950-1952, has now been given new, important and extensive responsibilities in his firm, and may not be able to devote time and energy directly to our Association and

Whereas Dr. Koppenhoefer is held in high esteem by the officers and members of the American Leather Chemists' Association and his past contributions are greatly appreciated;

Therefore, Be it Resolved, that the Council of the American Leather Chemists' Association does hereby acknowledge with great respect and appreciation, the many contributions made by Dr. Robert M. Koppenhoefer to the Association, to the scientific and technological advance of the Tanning and Leather Industry, to education and to his fellow men and does express the well wishes of all in his new position as Vice President and Director of Socony Mobil Oil Company.

It is Further Resolved, that this resolution be made of record by publication in our Journal.

EMPLOYMENT NOTICE

WANTED—Active member desires position involving responsibility. Proven ability to function under pressure in sales, administration, or production spots. The chances are that you know of me and my record. Please reply to Box A-16, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

THE COVER

The beginnings of the Leather Industries Research Institute of South Africa go back to 1935, when the present Director, Professor S. G. Shuttleworth, prepared a thesis for the M.Sc. degree in the Department of Chemistry of Rhodes University, under the guidance of Professor W. F. Barker. From this modest beginning the Institute's staff has grown to an even two dozen: one Director, three Senior Research Officers, eight Research Officers, and a nongraduate staff of twelve. In proportion to the population of the country and to the output of the industries served, no country in the world is spending as much on leather research as is South Africa. The Institute has an income of approximately £50,000 per annum, derived from guaranteed five-year grants from the footwear, tanning, hides and skins, and wattle industries, which grants are matched pound for pound by government funds. Additional financial support is derived from patent royalties and fees for services.

From this Institute has come a flow of very worthwhile papers on many phases of leather chemistry. Many of these have been published in this *Journal.*

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The Secretary announces acceptance of the following new members:

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R. H. Bacon, R. H. Bacon & Company, 14 East Jackson Blvd., Chicago 4, Illinois.

William C. Beier, Buffalo Extract & Supply Company, Inc., 717 Elk Street, Buffalo 10, New York.

L. P. Breithaupt, Breithaupt Leather Company, Adams Street, Kitchener, Ontario, Canada.

Everett T. Cole, Jr., P. O. Box 82, Napa, California.

Thomas E. Curtis, Fouke Fur Company, 1328 South Kingshighway, St. Louis 10, Missouri.

Gerald J. Desmond, Jr., 73 Rutland Road, Glenrock, New Jersey.

Willis D. Dicome, Dow Corning Corporation, Midland, Michigan.

Herbert Doberthien, 544 Dunbar Road, Kitchener, Ontario, Canada.

Thomas L. Dorrian, 5356 Madison Avenue, Skokie, Illinois.

Frederic L. Ekstrand, 926 Carleton Road, Westfield, New Jersey.

Charles L. Flooding, 900 Bush Avenue, St. Paul, Minnesota.

Frank Glazer, Jr., 3123 N. Twelfth Street, Sheboygan, Wisconsin.

Robert G. Henning, 656 – 13th Street, Oakmont, Pennsylvania.

Peter S. Kehayes, 634 Dorseyville Road, Pittsburgh 38, Pennsylvania.

Robert D. Kelley, 1303 - 17th Avenue, South Milwaukee, Wisconsin.

James M. Kelly, 167 So. Main Street, Gloversville, New York.

Miguel A. Liscano V., Ave. H #3-33, Cali, Colombia.

Carl J. Mahoney, 129 Brunswick Road, Cedar Grove, New Jersey.

Rodney G. Martin, 2522 Wilgus Road, Sheboygan, Wisconsin.

Emmett McGrath, Burk Brothers, 925 North Third Street, Philadelphia 23, Pennsylvania.

W. A. Miller, International Latex Corporation, Dover, Delaware.

Paul A. Oestreich, Western Leather Company, 904 East Person Street, Milwaukee 1, Wisconsin.

Francis Person, Koppers Company, Inc., Chemical Division, Box 65, Monaca, Pennsylvania.

D. W. Rappleye, Route #5, Shelbyville, Tennessee.

William C. Rosenbaum, Fouke Fur Company, 1328 South Kingshighway, St. Louis 10, Missouri.

Henry Schreiber, Apex Chemical Company, 200 S. First Street, Elizabethport 1, New Jersey.

Ralph E. Thompson, Ansul Chemical Company, 828 N. 29th Street, Philadelphia 30, Pennsylvania.

Joseph Wauters, c/o H. Schotte & Fils, Erembodegem, Belgium.

Henry D. Winer, 1 Ruby Terrace, Marblehead, Massachusetts.

A. O. Wingender, Ansul Chemical Company, Marinette, Wisconsin.

Robert F. Wise, Box 381, Campbellford, Ontario, Canada.

AUDIT REPORT OF ALCA

December 31, 1956

ARTHUR W. HOLMES
Certified Public Accountant

EXHIBIT I

BALANCE SHEET AT DECEMBER 31, 1956
AND COMPARISON WITH DECEMBER 31, 1955

	December 31, 1956	December 31, 1955
ASSETS		
Current Assets:		
Cash on hand	$ 24.16	$ 30.34
Cash in bank	16,007.48	13,830.46
Accrued interest on U.S.T. Bonds	62.50	100.00
Accounts receivable, Directory	47.00	560.00
Accounts receivable, advertisers	1,846.35	1,971.10
Accounts receivable, reprints	–0–	314.00
Total Current Assets	$17,987.49	$16,805.90
Investments:		
U. S. Savings Bonds, series F, at cost of $3,700 plus accrued interest of $670.00 at December 31, 1956	$ 4,370.00	$ 4,240.00
U. S. Treasury Bonds, 2½%, series of 1967-1972 at cost	28,495.00	28,495.00
U. S. Treasury Bonds, series G, 2½% due July, 1958 at cost	5,000.00	5,000.00
U. S. Treasury Bonds, 2½%, series of 1963-1968 at cost	8,842.50	8,842.50
Total Investments	$46,707.50	$46,577.50
Total Assets	$64,694.99	$63,383.40
LIABILITIES AND CAPITAL		
Current Liabilities:		
Accounts payable	$ 80.46	$ 378.50
Income tax withheld	194.80	218.80
City tax withheld	13.00	–0–
Total Current Liabilities	$ 288.26	$ 597.30
Deferred Credits to Income:		
Dues received in advance	$ 388.00	$ 439.50
Subscriptions received in advance	3,197.66	3,032.29
Total Deferred Credits to Income	$ 3,585.66	$ 3,471.79
Total Liabilities	$ 3,873.92	$ 4,069.09
Capital:		
Earned surplus (Exhibit III)	$58,821.07	$59,314.31
Reserve for foreign meetings	2,000.00	–0–
Total Liabilities and Capital	$64,694.99	$63,383.40

EXHIBIT II
STATEMENT OF INCOME
For the years ended December 31, 1956 and December 31, 1955

	December 31, 1956	December 31, 1955
Revenues, General:		
Dues, Journal subscriptions included	$11,489.01	$11,176.91
By-Laws and methods booklet	82.57	290.10
Directory	804.20	807.00
Interest income	1,205.00	1,167.91
Total General Revenues	$13,580.78	$13,441.92
Revenues, Journal:		
Advertising	$11,348.19	$12,057.45
Subscriptions	5,448.88	5,208.81
Journal sale	1,107.70	632.38
Reprints	1,388.49	1,745.94
Dues, I.S.L.T.C.	806.00	957.50
Total Journal Revenue	$20,099.26	$20,602.08
Total Revenue	$33,680.04	$34,044.00
Expenses, General:		
Secretary expense	$ 4,200.00	$ 4,200.00
Office operating expense	1,350.90	835.38
Uncollectible accounts expense	476.00	293.50
Directory expense	912.19	888.23
Annual meeting expense	218.07	449.14
Council meeting expense	84.35	54.50
Winheim award	–0–	100.00
Auditing	200.00	175.00
Leather Chemists Union dues	119.28	119.46
By-Laws and methods	361.35	1,535.99
Total General Expenses	$ 7,922.14	$ 8,651.20
Expenses, Journal:		
Printing	$18,082.43	$15,447.57
Editor's compensation	2,933.33	1,500.00
Editor's expense	536.43	463.94
Insurance	62.00	62.00
Storage	350.00	350.00
Miscellaneous	60.00	35.05
Copyright registration	48.00	48.00
Reprints	1,640.00	2,088.20
Exchange charges	1.05	.99
Translations and abstracts	305.08	249.95
Committee expense	109.25	81.00
Advertising discounts allowed	123.57	127.65
Total Journal Expense	$24,251.14	$20,454.35
Total Expense	$32,173.28	$29,105.55
Net Income	$ 1,506.76	$ 4,938.45
Distributed: General	$ 5,658.64	$ 4,790.72
Journal	(4,151.88)	147.73
Total	$ 1,506.76	$ 4,938.45

EXHIBIT III
STATEMENT OF SURPLUS

For the years ended December 31, 1956 and December 31, 1955

	December 31, 1956	December 31, 1955
Balance, January 1	$59,314.31	$54,375.86
Add: Net Income:		
General	5,658.64	4,790.72
Journal	(4,151.88)	147.73
	$60,821.07	$59,314.31
Deduct: Allocation to Reserve for Foreign Meetings	2,000.00	–0–
Balance, December 31	$58,821.07	$59,314.31

Until the middle of the seventeenth century, hangings, and even carpets, of decorated leather formed an important item in those inventories of princely possessions which are such a reliable and inexhaustible source of information for the historian of the sumptuary arts. Princes and other great personages depended largely on decorated leather and tapestries, when moving from place to place, to supplement the often hastily improvised decoration of their temporary apartments.
—*The Decoration of Leather.* Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

Leather manufactured [*in the early Middle Ages*] in Spain, Portugal, Flanders, and later in England is *almost* always decorated in high relief with touches of gold, the design being principally flowers, foliage, cupids, pomegranates, etc. Venice alone remained faithful to flat decoration with hollowed or merely darkened outline in the cameo-like medallions of classical scenes painted on groundwork whose design was borrowed from the gorgeous stuffs of the East.—*Ibid.*

Gilt leather hangings were at one time much sought after. Their qualities of being, unlike woollen and other materials, unaffected by damp and insects, of retaining their brilliancy unimpaired by time, of not attracting dust, and of allowing it to be easily removed by washing with a sponge, and finally, of not lending themselves to the multiplication of the insects which in summer infest the capital and which find in other tapestries convenient nests for depositing their eggs, were all advantages, forming so many reasons for their being in demand and gaining for them a place in the apartments of the great, of which they frequently constituted the ornament. But to-day, a change of taste and the dictates of fashion which outweighs even the advantages and conveniences of life, have caused them to be almost forgotten and relegated them to the ante-rooms of a few county houses where some of the earliest are to be found, nearly as beautiful as when they were first made in Paris.
—Preface written in 1762 by Fougeroux de Boudaroy, commissioned by the Academy to take over the work of research, previously conducted by Reaumur, on the subject of leather hangings, quoted in *The Decoration of Leather.* Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

ABSTRACTS

Influence of Some Organic Acids on Basic Zirconium Sulfate Solutions. M. P. Portes. *Bull. Assoc. Franc. Chimistes Ind. Cuir,* **18,** 71 (1956).—Zirconium tannage has become of steadily increasing importance. This paper is intended to define the effect of organic acids or their salts on the behavior of zirconium tanning solutions. Basic zirconium sulfate (42% Schorlemmer) was subjected to potentiometric titrations in presence of formic, acetic, and lactic acids. Without addition of the organic acids, the neutralization curve has no sharp inflection to indicate the existence of zirconyl sulfate; precipitation begins at a basicity of 62–64%; total precipitation corresponds with $(2\ ZrO_2–1\ SO_3)_n$; neutralization is complete before addition of the theoretical alkali equivalent because of precipitation of basic sulfates which decompose only slowly and in part because the formed precipitate always absorbs sulfuric acid. At this point, the basicity is 64% and the pH 2.9. The addition of acetic acid shifts the point of precipitation in accordance with the increased molar ratio of acid to Zr from pH 2.9 at 0 acetic acid to pH 5.2 at 2 moles acetic acid. The addition of lactic acid raises the precipitation point to pH>8 at a ratio of 1 mole acid—an effect more marked than in the case of acetic acid. In the case of formic acid, precipitation takes place at pH 3.5 with 1 mole acid, but more acid has no further influence. These results justify the assumption that acetic and lactic acid ions have a marked masking effect on zirconium, an effect which is shown only to a limited degree in the case of formic acid. Since hydrolysis of zirconium begins in the strongly acid range, with an irreversible affinity of basic zirconium toward collagen, drawn grain and slow penetration are frequent drawbacks of the zirconium tannage. By utilizing masked compounds, these defects disappear. Overtannage of the surface is eliminated and penetration becomes more rapid and more uniform. Electrochromatograms are presented showing the migration of basic zirconium by itself and in combination with acetic, lactic, and formic acids, as well as the migration of zirconium oxychlorid $Cl_2OZr \cdot 8\ H_2O$. Theories on the possible molecular structure of the zirconium salts in their changes from anionic to cationic compounds are discussed. T.D.B.

The Composition of the Strong Phosphoric Acids. A. L. Huhti and P. A. Gartaganis. *Can. J. Chem.,* **34,** 785–97 (1956); *Chem. Abstr.,* **51,** 926*b*. —Hexametaphosphoric acid is not a chemical entity.

The Use of Spectroscopy to Study Complex Formation in Solutions. S. A. Shchukarev and O. L. Lobaneva. *Vestnik Leningrad. Univ.,* **11,** No. 16, *Ser. Fiz. i Chem.,* No. 3, 64–73 (1956); *Chem. Abstr.,* **51,** 929*b*.

A Fibrous Keratin Precursor from the Human Epidermis. I. The Extraction and Physical Properties of a Fibrous Protein Found in Human Epidermis. D. A. Roe. *J. Invest. Dermatol.,* **27,** 1–8 (1956); *Chem. Abstr.,* **51,** 1333*f*.

Polyphosphate Tannage. Tanning Experiments with Various Polyphosphates and Their Fractionization Products. R. Lasserre. *Bull. Assoc. Franc. Chimistes Ind. Cuir,* **18.** 9 (1956).—A definition of the various poly-

phosphates marketed in France and best suited for pretanning is given. Analyses are presented, and an attempt is made to define the conditions required to make them useful as tanning agents. T.D.B.

Determination of the Wear Resistance of Sole Leather. H. Martin. *Bull. Assoc. Franc. Chimistes Ind. Cuir,* **18,** 22 (1956).—A description is given of the construction and operation of the Progil abrasion meter. To standardize the machine, disks of Plexiglass M 33 are used. While the rate of abrasion of Plexiglass is uniform throughout its thickness, leather shows a higher rate of wear for the initial 20–30% of its thickness, then slowing down to a constant wear. Abrasion is measured by the time necessary to wear away 4 mm. of leather on the machine; the value is extrapolated from a graph. It is suggested that Plexiglass M 33 should be used to determine the abrasion coefficients for the other various machines in use so that the results obtained for leather on these machines can be compared with the Progil machine. T.D.B.

Some Considerations on Physical Testing of Leather with Respect to Elongation. A. Kawamura and K. Wada. *Bull. Japanese Assoc. Leather Technol.,* **2,** 140–45 (1956) (English summary).—A test is described in which circular specimens are stretched in 6 directions successively, under a tension of 500 g., before and after tanning with various Cr compounds. The effect of the tanning agent is ascertained from the stretch after tanning. H.B.M.

The Bacteria Developing on the Culture Media Containing Hen's Dung. R. Sasaki, Y. Sato, and K. Nisikawa. *Bull. Japanese Assoc. Leather Technol.,* **2,** 126–32 (1956) (English summary).—Bacteria isolated from fermented fresh hen's dung at 37°C. were mostly gram-negative rods; from old dung, more gram-positive rods. Most strains of the latter digested gelatin, but only one strain digested elastin. Most of the gram-positive rods appeared to be *B. subtilis.* Cell-free extracts from one strain digested about 25% of the elastin from skin in 30 min. About 7% of the total skin N, exclusive of elastin N, was digested. The rate of digestion declined with time. H.B.M.

The Contribution of Scientific Research to the Tanning Industry. L. Del Pezzo. *Cuoio, Pelli, Mat. Concianti,* **32,** 339–46 (1956).—Progress in the tanning industry in the last half-century is reviewed with particular attention to the past and present organization of research and control work in Italian chemical laboratories. G.A.B.

Hair Problem (in Sewage Treatment). Anon. *Sewage and Ind. Wastes,* **28,** 1525 (1956).—Treatment plant operators who are plagued with the problem of tannery hair should be encouraged by the experience of Charles Hicks, superintendent of the disposal plant, Cobourg, Ontario, Canada. He reports that digester scum in his plant has been effectively controlled by the use of sludge recirculation and digester agitators. The Cobourg sewage treatment plant, in operation 6 years, receives a considerable quantity of hair from a local tannery. A fine revolving screen removes a large portion of the hair, although it is a considerable problem to keep the screen reasonably clean. Even with good operation some hair is pumped to the digester with the primary

sludge. If the accumulation of hair in the digester is not controlled, a heavy, matted sludge develops. Effective control has been obtained by recirculating the digester contents 2 or 3 times each week for a period of 3 hr. The sludge is pumped from the digester bottom and discharged in the top, while at the same time the high-speed digester agitator is operated. The agitator normally operates for 2 hr. out of every 6. The scum layer measures only 8″ and is not matted. Gas production is good and the sludge can be withdrawn readily to the drying beds. Odors resulting from the tannery wastes are controlled by chlorination of the raw sewage. J.F.W.

The Analysis of Hair Tints. I. Jacobelli-Turi. *Rendiconti Ist. Super. Sanitá, Roma,* **19,** 461–69 (1956).—The proposed methods may be used not only for hair tints but also for research in the field of fur dyes. The dyes may be detected chromatographically, and in this first report the data are given for several commonly used compounds. The values of R_f were determined by examining the chromatographic spots obtained using as solvent a 4:1:5 mixture of butanol, acetic acid, and water at 20°C. The R_f values are: *p*-phenylenediamine, 0.38; 2, 5-toluylenediamine, 0.48; *p*-aminophenol, 0.55; pyrogallol, 0.71; resorcinol, 0.83. As it may happen that several other compounds have R_f values very close to those indicated above (e.g., pyrocatechol, R_f 0.82), several color reagents were studied which may be used to identify the single constituents: (*a*) saturated (cold) aqueous solution of vanillin containing HCl (2.5 ml. per 100); (*b*) 0.5 g. of *p*-dimethylaminobenzaldehyde and 30 ml. HCl in 100 ml. H_2O; (*c*) 2 g. phenol in 100 ml. of 5% KOH containing 20 ml. of a dilute solution of Na hypochlorite; (*d*) 1 drop aniline in 250 ml. H_2O acidified with 10 ml. acetic acid and 3 g. Na persulfate; (*e*) 1% solution of silver nitrate. The sensitivity of these reagents permits the detection of the above indicated compounds at concentration of 0.2–0.5 γ per ml. G.A.B.

The Effects of Acids and Salts in Vegetable Tanning. I. The Effect of Some Salts in Chrome Leather Tanning. Y. Nayudamma, K. S. Jayaraman, and T. S. Krishnan. *Bull. Central Leather Research Inst., Madras,* **3,** 145–62 (1956).—Pieces of wet-salted buffalo hide were soaked, limed, dehaired, and thoroughly delimed with boric acid. Tannage was done with wattle, starting at pH 4.8 and 15°Bk. liquor and reducing the pH value by 0.2 and increasing the concentration by 15°Bk. every second day. Tanning time was 14 days. Three series of tests were run besides a control: (I) Pelt pretreated with 10% NaCl solution, alone or with addition of 5% of Na formate, acetate, citrate, lactate, oxalate, tartrate, dichromate, or Calgon, plus H_2SO_4 to give an equilibrium pH value of 4.8 after 36 hr.; tan liquors adjusted with H_2SO_4. (II) Pelt pretreated with 5% solutions of the above salts, without NaCl, plus the acid corresponding to the organic salt (H_2SO_4 in the cases of Calgon and $Na_2Cr_2O_7$); tan liquors adjusted with same acids. (III) No pretreatment, but the above salts were added to all the tan liquors (0.5% on hide weight or 0.1% by volume). Rate of penetration of tannin was accelerated by Calgon, and by Na citrate, acetate, oxalate, and formate; it was little accelerated by lactate and tartrate and not accelerated, or even retarded, by NaCl and $Na_2Cr_2O_7$. The effect was more marked in Series II than in Series I (NaCl present) and was less marked in Series III. In all cases shrink temperature rose to maxima at 4 to 8 days (87°–94°C.) and then declined to constant values

(81°–84°), with the final values slightly higher for stock pretreated with dichromate. Water-solubles content of the leathers was lowered when NaCl was used in pretreatment (Series I); the decrease was less marked in Series II and still less in Series III. Degree of tannage was lower in Series II than for the control, and somewhat higher than the control for Series II and III, but the distribution of tannin between grain, middle, and flesh layers was less uniform than for the control. The treatment with salts apparently gives more penetration of grease in oiling. The character of the experimental leathers was excellent, with generally better color than the control, especially for Series II leathers. Best color was obtained with Calgon and Na acetate. H.B.M.

Chromatographic Separation and Identification of Amines. M. Vecera and J. Gasparic. *Chemistry & Industry*, **1957**, 263.—Primary and secondary amines can be separated and identified by paper chromatography of their reaction products with 3:5-dinitrobenzoyl chloride (3:5-dinitrobenzamines), using filter paper impregnated with formamide. The mobile phase is a mixture of C_6H_6 and cyclohexane. The chromatogram is developed with alcoholic *l*-naphthylamine and observed under U.V. light. Separation can likewise be effected by column chromatography on Al_2O_3 with $CHCl_3$–C_6H_6 as eluting agent. H.B.M.

Studies on Insect Damage to Raw Hides.—By Larval Forms of *Anthrenus Vorax*. R. Bhaskaran, S. N. Sen, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **3**, 163–66 (1957).—The larva of the beetle *Anthrenus vorax* attacks the grain side of flint-dried and dry-salted hides, apparently feeding on hair and epidermis and creating denuded patches. In some cases the grain layer is consumed. The adult beetles do not attack hide. H.B.M.

Trends in Fat Liquors. F. J. Chadwick. *Shoe and Leather Reporter*, **285**, No. 2, 21 (1957).—The trend in fat liquors is from the cationic-nonionic emulsified fat liquors to the anionic system of fat liquors because of the ability of the latter to function over a wide temperature range and because changes in fatliquoring processes are more easily handled by the anionic system. A solubilized moellon shows considerable promise as an alternate for established fat liquors, as well as possessing entirely new uses in lubricating leather fibers. Another development (in plant experimental stage) shows promise of overcoming the spue potential of fatty oils. J.J.

Structure of Keratin. II. Amino Acid Content of Fractions Isolated from Oxidized Wool. C. Earland and C. S. Knight. *Biochem. et Biophys. Acta*, **22**, 405–11 (1956); *Chem. Abstr.*, **51**, 4004*c*.

Determination of Chromium Salts with Complexon (III). G. Doppler and R. Patzak. *Z. Anal. Chem.*, **152**, 45–52 (1956); *Chem. Abstr.*, **51**, 3357*b*.

Photometric Determination of Zirconium. H. Flaschka and M. Y. Farah. *Z. Anal. Chem.*, **152**, 401–11 (1956); *Chem. Abstr.*, **51**, 3363*a*.

Transverse Striations and Periodate-Silver-Urotropin Reaction with Different Collagens. H. Kühn, U. Hofmann, and W. Grassmann. *Z. Naturforsch.*, 11B, 581–88 (1956); *Chem. Abstr.*, **51,** 3690*d*.

Macromolecular Interaction Patterns in Biological Systems. F. O. Schmitt. *Proc. Am. Phil. Soc.*, **100,** 476–86 (1956); *Chem. Abstr.*, **51,** 3681*e*.

Histochemistry. XLV. Determination of Hydroxyproline in Microgram Amounts of Tissue. B. W. Grunbaum and D. Glick. *Arch. Biochem. and Biophys.*, **65,** 260–67 (1956); *Chem. Abstr.*, **51,** 3721*e*.

Study of Vegetable Tanning by Means of Modified Collagens and Polyamides. K. H. Gustavson. *Bol. Asoc. Quim. Espan. Ind. Cuero,* **16,** 67–78 (1954).—An address dealing with the reaction of typical vegetable tannins with polyamides and with natural or esterified collagen, and the influence of pH in the fixation of the tannins. J.B.B. and M.G.B.

Contribution to the Determination of the Isoelectric Point of Collagen. A. Staib. *Bol. Asoc. Quim. Espan. Ind. Cuero,* **16,** 79–88 (1954).—This paper is based on Loeb's work, which proved that the potential difference between a protein sol in a collodion bag and the exterior liquid media is zero. The electrosmosis method is used to confirm the results. Measurements were made when collagen was added to acid and alkaline solutions, and to the same solutions plus NaCl. The influence of swelling agents, as well as that of tannage, was also studied. A full description of the method, as well as tables and graphs of the results, is given. The author concludes that at the I. P. the collagen and medium are isoionic for H^+, which indicates that the I.P. depends on the dissociation constants of the acid and the collagen salt. The NaCl moves the I.P. to the acid side. The I.P. of collagen presents different values, depending on the nature of the swelling of the protein, and it is not a constant that defines its purity. The I.P. indicates a physico-chemical state of the protein. Its determination is very important, as it reveals the modifications introduced in the disposition of the protein macromolecule, and permits the identification of the functions of a chemical compound. It also reveals the state of the collagen in the unhairing and tanning operations, which constitutes another control method of regulating the quality of the product. J.B.B. and M.G.B.

Exchange Tanning Materials. W. O. Dawson. *Leather and Shoes,* **133,** No. 6, 82 (1957).—Exchange tannins are prepared from phenol or phenolic compounds. Under varying conditions of chemical treatment many different effects can be produced, such as degree of reactivity, filling, and softening effects. The advantages of using exchange tanning materials in the vegetable tan vats and as a chrome retan are listed. J.J.

New and Replacement Tanning Materials. F. A. Edmonds. *Weekly Bulletin, Leather and Shoe News,* **62,** No. 3, 5 (1957).—The author lists the replacement tanning materials as naphthalene and phenol base syntans, sulfone and sulfonamide syntans, resorcinol syntans, styrene-maleic anhydride compounds, the aliphatic sulfonyl chlorides, the isocyanates, the various amino resins, and Cr complexes formed with phenols and lignosulfonates. Limiting

himself to the amino-type resins, the author discusses the reaction of HCHO with urea, dicyandiamide, melamine, and guanidine, and lists the optimum conditions for the reactions. The desirable properties of a tanning resin are given. An excellent account is given of the use of resins in producing all-white leather and chrome-white leather. Mentioned also are the properties of leather produced by resin-HCHO-alum tannage, resin-Cr tannage, and retanning with resin. The problems that arise with resin tannage are also listed. J.J.

Proper Finishing Materials for Decorated Leathers. A. Turow. *Leather and Shoes*, **133,** No. 10, 17 (1957).—A discussion of the problems in decorating leather caused by not marking the type of finish used and improper use of finishes. J.J.

New Approaches to White Leather. I. C. Somerville. *Weekly Bulletin, Leather and Shoe News*, **62,** No. 9, 28 (1957).—The author reviews the methods and discusses the developments in the methods of producing white leather by HCHO, Al, Cr, syntans, Zr, and resin tannages. J.J.

Chrome Tanning and Fatliquoring. C. E. Retzsch. *Leather and Shoes*, **133,** No. 3, 13 (1957).—Leathers with wider range of properties and characteristics to meet the demands of the fashion markets can be produced by the selection of proper oils when fatliquoring the leather in the original tan bath, the retan bath, separate fatliquor bath, or combinations of any of these fatliquoring operations. J.J.

Nonionic and Cationic Applications. D. Meo. *Leather and Shoes*, **133,** No. 3, 14 (1957).—The advantages and disadvantages of nonionic and cationic materials are enumerated, together with the advantages they possess as auxiliary products. J.J.

The Effect of Acid and Salt Adjustment in E. I. Tannage with *Pithecolobium Dulce*. M. K. Udaya Varma, E. C. Mathew, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **3,** 110–14 (1956).—Specimens of cowhide, limed and delimed for E. I. tannage, were tanned with *P. dulce* bark extract, 15°Bk., containing Na_2SO_4 (40, 100, or 150 milliequivalents per liter), HCOONa (40–120 milliequivalents), or Na lactate (25–100 milliequivalents). All liquors were adjusted to pH 5.0 with lactic acid. After tanning, all the leathers were bleached and retanned with myrobalans. There was a slight improvement in color of the leathers tanned with the lowest concentrations of each of the 3 salts and no further improvement at higher salt concentrations. Addition of salt resulted in increased yield and firmness, decreased content of tannin and water-soluble matter, and decreased shrink temperature. All these effects were very small. H.B.M.

The Use of Antiseptics in the Process of Soaking. I. Studies on Sodium Pentachlorophenate. R. Bhaskaran, S. N. Sen, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **3,** 115–20 (1956).—The Inhibition Coefficient (concentration of C_6Cl_5ONa required to inhibit bacterial growth) was determined for mixed cultures from soak waters. The inhibiting concentration was higher when pieces of hide were added to the broth culture medium

and increased with temperature and time of incubation. A concentration of 0.075 g. per 100 ml. is recommended for soaking 24–36 hr. at temperatures prevailing in India (29°–32°C.). H.B.M.

Studies in Chrome Tanning. II. Determination of Basicity of Chrome Liquors. Y. Nayudamma, K. S. Jayaraman, and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras*, **3,** 121–24 (1956).—The Lehigh Method and the Official Method for determining basicity were applied to 33% basic chrome liquor to which was added 0.5 to 5 moles of acid per mole Cr. The acids studied were aminoacetic, chloroacetic, citric, formic, glycolic, oxalic, tartaric, HCl, and H_2SO_4. From the data obtained, the authors conclude that neither method gives correct results in the presence of excess acid. H.B.M.

Contribution to the Study of Silica Tanning. P. Chambard and R. Lasserre. *Bol. Asoc. Quim. Espan. Ind. Cuero*, **15,** 54–61 (1954).—The subject is treated under the following aspects: (1) history; (2) tanning properties of the acid sols of silica in relation to their stability, concentration, and pH; (3) effects of the fixation of the silica (blockage of certain reactive groups of collagen); (4) trial of combined tannages with silica and vegetable or mineral tanning agents (Cr, Fe, Zr, polymetaphosphate); (5) possible reactions between the silica sol and the skin, and theory of silica tannage. A sol of a diluted solution of Na_2SiO_3 in a mixture of conc. HCl and acetic acid containing 2.5% SiO_2 was used. For maximum fixation, it is necessary to use a concentration of 15% SiO_2 on limed-weight basis, but the maximum fixable percentage of SiO_2 is almost reached from a concentration of 10%. The speed and percentage of fixation of this tannage are between those of the vegetable and chrome tannages. Best results were obtained with these sols when they were 48 hr. old, and with a pH of 2.6–3.2. Tests with deaminated skins showed a very slight decrease of the percentage of fixed SiO_2, which proves that the fixation of silica does not take place with the free amino groups only; other combinations can take place. J.B.B. and M.G.B.

Some Remarks on Resin Tannage in Europe. G. Mauthe. *Leather Mfr.*, **74,** No. 2, 27 (1957).—The author cites the characteristic differences between European and U. S. chrome leather. He lists 4 types of resin tanning agents: (1) water-soluble condensation products of urea or melamine or their derivatives with HCHO, which still contain reactive methylol groups; (2) nitrogen-containing water-soluble compounds, chiefly dicyandiamide derivatives with basic amino groups; (3) organic compounds containing amino and phenolic hydroxy groups which are kept in aqueous suspension by dispersants; and (4) dicyandiamide-HCHO resins, insoluble in water, which can be dissolved by the addition of naphthalene sulfoacid-HCHO condensation product. He explains in detail how the resin retanning operation and fatliquoring are carried out on chrome side leather, and gives a short discussion of resin retannage for other types of leather. J.J.

Comparative Study of the Different Methods of Tannin Analysis. Report of the Analysis Committee of the AQEIC. A. Torner Ochoa, R. Pagans Llauro, A. Yague Gil, J. Boleda Vila, J. Boix Carreras, J. L. Prieto, and A. Rodriguez Socorro. *Bol. Asoc. Quim. Espan. Ind. Cuero*, **14,** 4–16

(1954).—A series of nontannin determinations was made by the filter method, shake method, and direct detannization method, in 6 different vegetable tanning substances, by 6 different analysts, and the results were statistically interpreted. The authors could not find notable differences in the precision of the methods, although they found a lower dispersion of results in the direct detannization method which they think is due to better operational facilities of this method. Tables showing the results of the analysis, as well as the complete statistical study, are given. J.B.B. and M.G.B.

Formation of Resinous, Gummy Substances in Sumac Extracts by Alteration of the Nontannins. A. Yague Gil. *Bol. Asoc. Quim. Espan. Ind. Cuero,* **15,** 35–42 (1954).—The author makes a careful study of the variations of the composition of sumac extracts obtained and treated under different conditions (aqueous alcohol or water extractions, detannization, etc.). He finds that in an extraction with aqueous alcohol (1:1) the relation T/NT is higher than in a water extraction, with a much smaller amount of sugars and an absence of resins and gallic acid, and also a smaller alteration of the solutions. The nontannins form resinous, gummy substances which are known to be formed from the sugars. Hides tanned with an aqueous alcohol extract were of normal aspect, whereas hides tanned with a water extract, rich in sugars and containing gallic acid, were firm and showed a much darker color

J.B.B. and M.G.B.

New Chromatographic Method by Disks and Its Application to the Qualitative Investigation of the Tannins. A. Jamet. *Bol. Asoc. Quim. Espan. Ind. Cuero,* **15,** 43–46 (1954).—In a previous publication (Abstr., *JALCA,* **48,** 638 [1953]), the author described a method of chromatography on alumina disks and gave the results obtained on its application to the qualitative identification of tannins. The chromatographs obtained however, were weak and could be conserved for only a few days. He proposes a new method using paper. The results are more permanent and can be observed, with the help of a Wood lamp, after a few months. A filter paper (Whatman No. 1 or No. 4), is placed between the glass plate support and the alumina disk. The chromatographs on the paper and on alumina are not always identical, but the difference is another characteristic of the tanning material under study. A full description of the method is given, as well as the characteristics of the chromatographs of chestnut, oak, myrobalans, quebracho, wattle, mangrove, sumac, and gambier.

J.B.B. and M.G.B.

CORRECTION

In the paper "Penetration of Wattle Tannins into Hide as Examined by Chromatographic and Molecular Weight Methods", by D. G. Roux and S. R. Evelyn [*JALCA,* **52,** 58 (1957)], the third paragraph on page 64 should read as follows: "Molecular weights of the methylated tannins were determined with the modified Ray ebulliometric apparatus (4). The average molecular weights of the tannins themselves, given in Table I, were calculated from the molecular weights of the methylated tannins and their individually determined methoxyl contents(5)."

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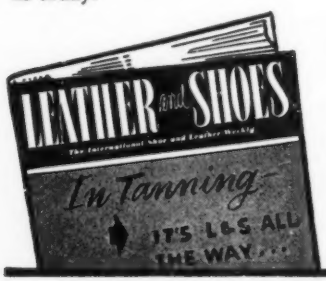

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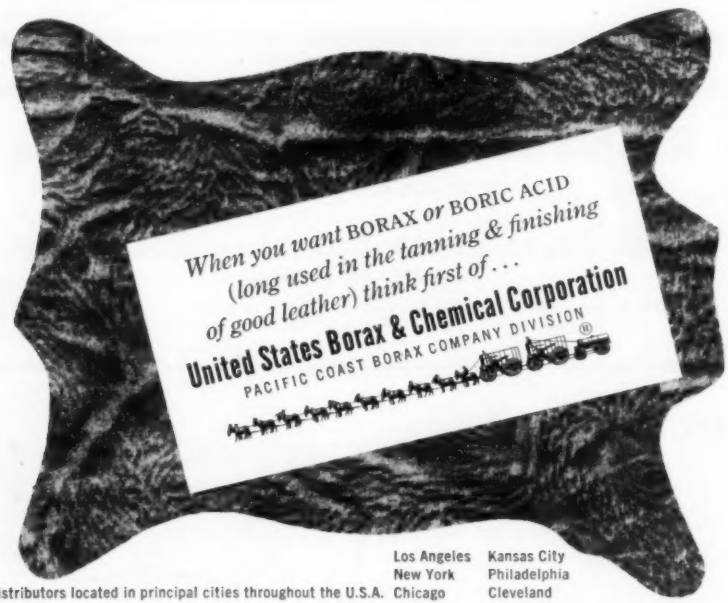
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